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ACID AEROSOL MEASUREMENT WORKSHOP

February 1-3, 1989
Research Triangle Park, North Carolina

FINAL REPORT

Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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FINAL REPORT

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ADS – annular denuder system
AES – Atmospheric Environmental Service (Canada)
AIHL – Air and Industrial Lab (California)
AREAL – Atmospheric Research and Exposure Assessment Laboratory
ATR – attenuated total reflectance
BNL – Brookhaven National Laboratory
C x T – concentration multiplied by time
CAPMoN – Canadian Precipitation Monitoring Network
CARB – California Air Resources Board
CASAC – Clean Air Science Advisory Committee
C – concentration
D_{50} – particle diameter for which the particle collection is 50% (also called 50% cut point)
DDM – denuder difference method
DEC – Department of Environmental Conservation (New York)
DOAS – differential optical absorption spectrometry
DQO – data quality objective
ECAO – Environmental Criteria and Assessment Office
EPA – Environmental Protection Agency
EPRI – Electric Power Research Institute
FM – frequency modulation
FPD – flame photometric detector
FTIR – Fourier transform infrared (spectroscopy)
IAA – infrared aerosol analyzer
IC – ion chromatography
IR – infrared
km – kilometer
LDL – lower detection limit
LOEL – lowest observed effect level
lpm – liters per minute
μg/m^3 – micrograms per cubic meter
μm – micrometer
MDL – minimum detectable limit
ml – milliliter
MMD – mass median diameter
mm – millimeter
M – molar
NAAQS – National Ambient Air Quality Standard
NEM – NAAQS Exposure Model
nequiv/m^3 – nanoequivalents per cubic meter
ng – nanogram
nmol – nanomole
nmol/m^3 – nanomoles per cubic meter

N – normal
NYU – New York University
OAQPS – Office of Air Quality Planning and Standards
OEN – Operational Evaluation Network (EPRI)
PAN – peroxyacetyl nitrate
PM – particulate matter
PM-10 – particulate matter $\leq 10\ \mu m$
PM-15 – particulate matter $\leq 15\ \mu m$
PM-2.5 – particulate mattter $\leq 2.5\ \mu m$
ppb – parts per billion
ppm – parts per million
QA – quality assurance
QC – quality control
σ_g – geometric standard deviation
SCAB – South Coast Air Basin
SCAQS – Southern California Air Quality Study
SOP – standard operating procedure
TAT – tungstic acid technique
TDLAS – tunable diode laser absorption spectroscopy
TFR – transition flow reactor
T – time (of exposure)
UC – University of California

SYMBOLS

H^+ – hydrogen ion, hydronium ion
H_2SO_4 – sulfuric acid
HNO_2 – nitrous acid
HNO_3 – nitric acid
N – nitrogen
NaCl – sodium chloride
NH_3 – ammonia
NH_3^- – ammonia gas
NH_4 – ammonium
NH_4^+ – ammonium ion
$(NH_4)HSO_4$ – ammonium bisulfate
NH_4NO_3 – ammonium nitrate
$(NH_4)_2SO_4$ – ammonium sulfate
NO_2 – nitrogen dioxide
NO_2^- – nitrite
NO_3^- – nitrate
HONO – nitrous acid
NO_x – oxides of nitrogen
O_3 – ozone
SO_2 – sulfur dioxide
SO_4^{2-} – sulfate

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SECTION 1

EXECUTIVE SUMMARY

INTRODUCTION

This report documents the results of a workshop on acid aerosol measurement methods sponsored by the Atmospheric Research and Exposure Assessment Laboratory (AREAL) of the U. S. Environmental Protection Agency (EPA). The workshop responds to a specific request by the Clean Air Science Advisory Committee (CASAC) that EPA use the mechanism of an expert workshop to obtain agreement within the scientific community on issues surrounding the characterization of aerosol acidity and acid aerosol measurement methods.

CASAC recommended in a 1988 report to EPA Administrator Lee Thomas that the evaluation of methods was a fundamental first step in a coordinated research program required to determine the need for a National Ambient Air Quality Standard (NAAQS) for acid aerosols. The report concluded that:

> The foundation of any air quality standard is the measurement method, not only because the standard itself must specify the method, but equally important, because before establishing a standard, the contaminant must be fully characterized and exposure measurements made to correlate with health outcomes. Therefore, it is critical to have measurement methods which have been thoroughly validated. . . . This [need to validate measurement methods] is especially acute with respect to the development of an acid aerosol standard.

Responding to the CASAC recommendations, the workshop was structured to accomplish two principal objectives. The first was to identify those species that should be emphasized in characterizing aerosol acidity. The second was to recommend protocols for an evaluation of current acid aerosol measurement methods that would quantify the accuracy and precision of their measurements. The workshop was attended by 72 participants including national experts in acid gaseous and aerosol measurements, two CASAC members, health effects researchers and NAAQS experts from EPA's Office of Air Quality and Planning Standards.

CONCLUSIONS

In evaluating acid aerosol species that should be measured, workshop participants concluded that the most appropriate indicator of aerosol acidity is fine particle strong acidity measured as hydrogen ion by either pH or titration. An accurate and reliable method that is free of possible interference was identified as an important initial research objective. This finding is consistent with the CASAC observation that currently observed significant health effects are associated with respirable fine particles and not with gaseous acids such as nitric and hydrochloric acid.

After considering procedures for evaluating current acid aerosol measurement methods, workshop participants concluded that the evaluation process must include (1) distribution of audit standards to check the accuracy and precision of laboratory analyses used in acid aerosol measurements, (2) tests of sampling and analysis systems using laboratory-generated aerosols with known composition and interferences, and (3) one or more field tests of the complete acid aerosol sampling and analysis system. Priorities for both laboratory and field evaluations should be: (1) quantifying the performance of methods currently used in epidemiology studies to ensure that measurements conducted by different groups will be comparable, and (2) completing the laboratory and field studies before the end of calendar year 1990.

THE WORKSHOP REPORT

The remainder of this report is divided into 12 sections. Section 2 provides background information on the CASAC recommendations that led to this workshop. Sections 3 - 12 summarize the presentations and discussions of the acid aerosol experts. Section 13 summarizes the workshop conclusions and recommendations. Finally, the workshop agenda, a list of the participants, assignments for group discussions, and summaries of the acid aerosol methods used in current epidemiology studies are appended.

SECTION 2

INTRODUCTION

The U. S. EPA sponsored the Acid Aerosol Measurement Workshop, February 1-3, 1989, in response to recommendations by CASAC concerning the need to evaluate and standardize acid aerosol measurement methods. Establishing standardized methods is an initial step in a coordinated acid aerosol research program addressing the possible listing of acid aerosol as a criteria pollutant. National experts and program managers, both outside and inside EPA, were invited to the workshop to review current acid aerosol measurement methodologies and to consider their applicability for ongoing exposure assessment and epidemiological studies. The agenda of the workshop was designed to address two principal objectives: (1) the identification of appropriate indicators and methods for the measurement of acid aerosols, and (2) to plan laboratory and field comparison studies of acid aerosol methods currently in use.

BACKGROUND INFORMATION

Section 109 of the Clean Air Act as amended requires EPA to develop and review NAAQSs as well as the scientific information and data on which they are based. New pollutants are to be listed for NAAQS development if the Administrator concludes that they may reasonably be anticipated to endanger the public health or welfare.

To assist the EPA Administrator in evaluating the need for new or revised NAAQSs, the Clean Air Act created CASAC. This committee's mandate is to provide the Administrator with scientific advice and research recommendations on critical areas of knowledge required in the NAAQS decision-making process. On October 6, 1988, the CASAC Acid Aerosol Subcommittee recommendations were approved with minor changes by the full CASAC and transmitted December 1988 in a letter to Administrator Lee Thomas.

The CASAC recommendations identify the need for a coordinated acid aerosol research program in characterization and exposure assessment, animal toxicity, human exposure research, and epidemiology. The CASAC indicated that the evaluation of acid aerosol measurement methods is a fundamental first step in this coordinated research program. The reason for this focus is found in the CASAC report (CASAC, 1988):

> The foundation of any air quality standard is the measurement method, not only because the standard itself must specify the method, but equally important, because before establishing a standard, the contaminant must be fully characterized and exposure measurements made to correlate with health outcomes. Therefore, it is critical to have measurement methods which have been thoroughly validated. . . . This [need to validate measurement methods] is especially acute with respect to the development of an acid aerosol standard.

CASAC recommended that EPA's Office for Research and Development (ORD) implement six high priority research objectives to acquire knowledge that it considers to be fundamental in acid aerosol characterization and exposure. These six objectives are:

1. The establishment of standard methods so that research and monitoring conducted by different groups will be comparable. This requires a program to evaluate, and to improve as needed, existing methods currently being used outside EPA to collect exposure, health, and ambient characterization data.

2. The evaluation of those species that should be emphasized in characterizing aerosol acidity as well as determining which are the best candidate measurement methods currently available. CASAC indicated that this evaluation should include EPA sponsorship of a workshop of national experts to consider these issues.

3. The field testing, comparison, and data analysis of current acid aerosol and ammonia measurement methods. This will require detailed planning and preparation as well as close coordination with the National Oceanic and Atmospheric Administration, which currently is conducting an ammonia methods "shootout."

4. The evaluation of the results of the methods testing and comparison programs in a second workshop to determine the causes and remedies for differences among these methods. This workshop should address also ammonia measurement methods and should be completed before further field studies begin.

5. The spatial and temporal characterization of acid aerosols and gaseous ammonia. This will require detailed monitoring in five or six urban areas in the United States and should include indoor as well as outdoor measurements.

6. The estimation of population exposure to acid aerosols in all microenvironments. This will require the evaluation of current exposure models, particularly the NAAQS Exposure Model (NEM), before outdoor and indoor studies are designed and implemented to ensure that collected data satisfy the requirements of the models.

In response to CASAC's December 1988 letter to Lee Thomas, EPA's AREAL sponsored the Acid Aerosol Measurement Workshop that was prominent among the committee's recommendations. The February 1989 workshop was attended by national experts in aerosol measurement and by two CASAC members as well as by health effects researchers and NAAQS experts from OAQPS.

The workshop was designed to solicit detailed information about several of the high priority characterization and exposure objectives identified in CASAC's research recommendations. Specifically, workshop participants were asked to consider:

- species that should be measured to characterize aerosol acidity,
- whether current measurement methods could be suitable candidates for best measurement techniques, and
- design recommendations for field testing and comparison of measurement methods.

OPENING REMARKS

At the workshop, Dr. William E. Wilson of EPA described how CASAC, in reviewing material prepared to support revising ambient air quality standards, felt there was evidence of potential adverse health effects that could be linked to acid aerosols. The CASAC subcommittee formed to look into the issue felt there was sufficient indirect evidence of potential adverse health effects to recommend additional research be conducted to determine the health effects of acid aerosols, evaluate measurement methods and improve them as needed, characterize the spatial and temporal behavior of acid aerosols, and estimate population exposures. Ultimately, these research efforts would lead to a decision concerning whether or not to list acid aerosol as a criteria pollutant and establish an NAAQS.

Wilson noted that the first objective is to establish a standard measurement method. If the decision is eventually made to list acid aerosol as a criteria pollutant, then a standard will have to be promulgated in the Federal Register. In reviewing measurement methods, several outcomes are possible:

- None of the current methods is suitable, in which case new techniques would need to be developed.
- A current measurement technique is sufficient to adopt as a standard now.
- Several current techniques may be suitable, but there are some differences among them, in which case a comparison study would be warranted.

He concluded by stating that EPA is seeking attendees' assistance in establishing a measurement method.

SECTION 3

REVIEW OF ACID AEROSOL HEALTH EFFECTS DATA

Dr. Judith Graham with EPA's Environmental Criteria and Assessment Office (ECAO) gave an overview of the health effects of acid aerosols. She noted that although the data base is sparse, some data do exist. In general, for every positive study there is often a negative one. Although there is reason for concern about the health effects of acid aerosols, there is insufficient information for a quantitative risk assessment. The charge of this workshop is an important initial step in achieving quantitative risk assessment. The discussion of the health effects of acid aerosols was divided into two categories, acute effects and chronic effects.

ACUTE EFFECTS

Much of the early knowledge of acid aerosols comes from epidemiology studies with insufficient or no acid aerosol measurement. Classic mortality studies in the Meuse Valley, London (1952), and Denora, PA, showed large increases in mortality affecting primarily the elderly and those with preexisting respiratory and cardiovascular disease. Unfortunately there were no adequate measurements of acid, but high levels of acidity are suspected. A later episode in London (1958-59) has recently been reanalyzed and a preliminary estimate obtained for the correlation between mortality and the log of sulfuric acid. This yielded at least some presumptive evidence that high ambient levels of acidity have been associated with mortality.

Studies of lung pathology in animals have shown no effects at low levels ($<1000\ \mu g/m^3$). After acute exposure, effects on pulmonary function have been observed. Pulmonary function is one indicator of a range of effects that occurs with various air pollutants. Recent epidemiology studies, particularly a recent series of summer camp studies, have evaluated the effects of ambient air pollutants on children. These data are still being reanalyzed, but effects have been observed that are associated with ozone. However, ozone does not appear to be the sole factor in the observations. It is possible that additional pollutants present, particularly acid aerosols, may have contributed to the effects of ozone.

With controlled animal toxicology and human clinical studies, it is easier to determine precise cause and effect relationships. Pulmonary effects have been observed after 1-hour acute exposures including narrowing of airways and stiffening of lungs. The lowest observed effect level (LOEL) for one study on guinea pigs was 110 $\mu g/m^3$ of sulfuric acid for 1 hour. The investigators obtained a potency ranking where sulfuric acid > ammonium sulfate > ammonium bisulfate. This particular ranking, however, has not been observed for other end points by other investigators. Almost all the acid aerosol studies under controlled situations on humans and animals have been done with sulfuric acid, so little is known about other acid species such as nitric acid or hydrochloric acid.

Few clinical studies of normal human subjects exposed for 1 hour to sulfuric acid showed any effect in pulmonary function at levels up to 1000 $\mu g/m^3$. For the few studies that did report symptoms (such as cough and throat irritation), levels were around 1000 $\mu g/m^3$ sulfuric acid.

More recently, attention has shifted to the study of asthmatics. There have been a variety of studies of the pulmonary function of asthmatics including a wide range of disease status, exposure modes, and exercise levels. These studies indicate that generally an adverse effect occurs as acid aerosol concentration increases. Thus, compared to studies on normal subjects, asthmatics are affected. However, the wide scatter in the data probably reflects the variety of study designs. Some studies that showed effects at fairly low levels were done with adolescent asthmatics. Some effects were seen at about 1000 $\mu g/m^3$ sulfuric acid, yet other studies show little or no effect. The data base is just emerging and is insufficient to draw quantitative conclusions. Qualitatively, asthmatics are more sensitive than normal subjects to acute effects of sulfuric acid.

Lung reactivity to bronchoconstricting drugs is also an end point used in clinical studies to illustrate sensitivity of airway receptors to provocative agents. Again, at low levels (100 $\mu g/m^3$) no effects are seen, at high levels (1000 $\mu g/m^3$) effects are fairly clear. At intermediate levels (450 $\mu g/m^3$), investigators have observed differences between normal subjects and asthmatics. The effects on normal subjects were immediate, while effects on asthmatics came 24 hours after exposure.

The lung has many ways to defend itself against both viable and nonviable substances. In this case, when the ability of the lung to defend itself against bacteria was investigated, no effects were observed in a classical model. However, investigators have discovered recently that subchronic exposures (500 $\mu g/m^3$, intermittent, 13 days) cause a decrease in the ability of lung cells to take up particles.

Another primary effect of acid aerosols that interests health effects researchers is clearance from the lung. There are two main types of clearance mechanisms: one occurs in conducting airways where nasociliary clearance is a fairly rapid process; the other occurs deeper in the lung at the alveoli where gas exchange occurs. This alveolar clearance is a slower process with different mechanisms participating. In the conducting airways high up in the main windpipe, no effects have been observed, but nasociliary clearance has been affected in similar ways in both animals and humans.

It appears that the higher the actual dose delivered to the target tissue, the greater the tendency for clearance to slow. Sometimes, at low concentrations and brief exposure duration, clearance increases. The ambient aerosol particle size is a very important factor in observing and interpreting effects. For rabbits, a potency ranking is obtained that is consistent with the potency ranking for asthmatics: sulfuric acid > ammonium bisulfate > ammonium sulfate, sodium sulfate. With human studies, very similar effects are observed; the LOEL is about 100 $\mu g/m^3$ for 1-hour exposures where slowing was observed in the small conducting airways of normal subjects. In one study, after a 1- and 2-hour exposure the decrease in clearance became worse after doubling the exposure (100% decrease after 1 hour, 162% decrease after 2 hours). In addition, the recovery from this effect was slowed at 2 hours. With alveolar clearance (in animal studies only), a similar pattern of effects is seen depending upon the range. At 250 $\mu g/m^3$, clearance accelerates; as dose increases, clearance slows. The data base on alveolar studies is still emerging; there have only been one or two studies in this area.

CHRONIC EFFECTS

The other main category of effects is chronic effects. Lung structure has been examined in several animal studies. However, only two major studies were discussed. In one, rabbits were exposed to sulfuric acid particles at a concentration of 250 $\mu g/m^3$, 1 hour a day, 5 days a week for 1 year (future studies will use lower concentrations and determine the LOEL). Among the more interesting effects concerning lung structure was an increase in cells that secrete mucus and fluids into the lung. These cells extended deeper into the lung where they normally do not occur. This was observed after only 1 month of exposure and the effect persisted 3 months after the 1-year exposure ended. In humans, this would be associated with a pathological state. The number of smaller airways also increased. Similar effects are observed after chronic exposure to cigarette smoke in humans. Studies conducted many years ago found effects on monkeys (380 $\mu g/m^3$ sulfuric acid for 23 hours a day for 78 weeks) that had similarities with more recent rabbit studies, i.e., cellular changes in the small airways.

Pulmonary function effects from sulfuric acid particles have been observed in dogs, donkeys, and rabbits. Older studies have shown decreases in lung volumes and increases in resistance, frequency, and hyperresponsiveness. The LOEL for pulmonary function was at a concentration of 900 $\mu g/m^3$ (for 21 hours per day for 620 days) in dogs; the LOEL for hyperresponsiveness occurred at 250 $\mu g/m^3$ (for 1 hour per day, 5 days per week, for 4 months) in rabbits. Some pulmonary function effects in rabbits were correlated with pathological effects, and there were effects on nasociliary clearance after chronic exposure. Effects have been seen at very low levels in both rabbits and donkeys; a persistent slowing was observed.

From epidemiology studies, one can only speculate and gather suggestions from the particulate sulfate data bases about morbidity. The Harvard six cities study data showed prevalence of bronchitis was correlated with increasing levels of particulate matter $\leq$ 15 μm (PM-15). Hydrogen ion concentration data were taken 2 years after the health measurements were made. Elevated acid levels are suspected at the time the health levels were determined. Although separation of the health and exposure measurements is a major caveat, the increasing prevalence of bronchitis with increasing hydrogen ion concentration is noteworthy. An interesting hypothesis is that sulfuric acid may cause chronic bronchitis. Although direct evidence is lacking, correlations of effects from sulfuric acid and cigarette smoke in donkeys, humans, and rabbits suggest the plausibility of this hypothesis.

SECTION 4

OVERVIEW OF CASAC RESEARCH RECOMMENDATIONS

Dr. Morton Lippmann of New York University (NYU) reported that the CASAC recommendations for future research on acid aerosols were influenced by selected studies of the health effects of acid aerosols. The process began with the particulate matter (PM) and sulfur oxides standards review started in 1979. In 1981, CASAC concluded that the criteria document and the staff paper for PM provided a suitable scientific basis for proceeding. In 1984, the EPA Administrator published in the Federal Register a proposal for a PM standard and asked for public comment. CASAC met in 1985 to review the public comments and offer comments on the Administrator's proposal. It was noted that the data base was 4 years old and that much relevant data had been obtained in the interim. As a result, an addendum was prepared for both documents, reviewed, and recommended as suitable for the standard-setting process by CASAC in 1985. By 1987, the PM standard was finally promulgated. At the 1985 closure on the criteria document and staff paper update, CASAC noted that there was increasing evidence from the new data that the hydrogen ion content of the PM was a likely causal factor for the PM effects. Thus, CASAC asked EPA to prepare an issues paper that would bring forward and evaluate all of these data. In reviewing the issues paper in June 1988, CASAC made its recommendations.

To understand the basis for CASAC's recommendation, one must consider the results of the first study done on the effects of sulfuric acid aerosols in humans. The clearance of particles from the lung following a 1-hour exposure (at 100 $\mu g/m^3$ sulfuric acid) in a healthy resting person showed a marked acceleration. At higher concentrations, clearance slowed. More recently, studies have shown not only an effect, but one that lasted at least for several hours. With a 2-hour exposure at the same concentration, the effect was greater and persisted longer.

When interpreting results, it is important to realize that concentration alone is not adequate as a measure of exposure; an exposure dose is some function of concentration and time. Referring to an effect at some concentration is not appropriate.

A study of the response of rabbits showed the same effect, an acceleration of clearance at low dose becoming a slowing at higher doses. This effect is consistent with stimulating mucous secretion and occurred with a 1-hour exposure. In the rabbit, the data for 1-, 2-, and 4-hour exposures, expressed as the product of concentration and time (C x T), shows good consistency. Although the ambient concentration may not reach 100 $\mu g/m^3$, the ambient C x T product may very well exceed the exposure of 100 $\mu g/m^3$ for 1 hour used in the laboratory. Thus, these data are relevant to real current exposures in the summertime in the eastern United States.

A study of chronic effects showed that control rabbits exhibit no change in their clearance during a one-year sham exposure and 3 months of follow-up. However, those animals exposed daily for 1 hour a day at 250 $\mu g/m^3$ showed initially a slowed clearance and attempts at adaptation. At the end of the exposure, not only was there persistence, but it was worse because of the loss of the stimulus to clearance as well as the accumulated damage expressing itself. Although the rabbit is a good model, it is three times less sensitive than the human. It could be extrapolated that these effects would appear in a human at about 100 $\mu g/m^3$ for 1 hour a day. Also, the animals became more reactive to other stimuli. In this case, it was an acetylcholine challenge; however, it could be an antigen or ragweed or anything that could stimulate the lung. Clearly, the sulfuric acid made the lung more responsive.

The other study examined a single 3-hour exposure of guinea pigs to zinc oxide particles coated with sulfuric acid (so that the sulfuric acid concentration was 30 $\mu g/m^3$). There were effects on total lung capacity, vital capacity, functional residual capacity, and carbon monoxide diffusing capacity. These effects lasted as long as 72 hours after the single exposure. Similar data may be obtained with pure sulfuric acid, but it takes about 10 times more acid to get this effect. Additional work with a 3-hour exposure per day for 5 days shows effects at lower concentrations. This suggests that primary ash particles (similar to zinc oxide particles) coated with sulfuric acid may be more potent than secondary sulfuric acid (which is more like the pure acid droplet typically used in the laboratory).

In a version of the Harvard six cities study, there is a clearer relationship between bronchitis prevalence in 10- to 12-year-old children and acid than any other particle measure. There is certainly no effect with sulfur dioxide per se. Effects in humans are consistent with the animal data.

CASAC's judgement was that none of these effects or studies can stand up to scrutiny by themselves; every one can be criticized. Yet, there is a consistency and a weight of evidence for acid having causal effects on health that led the committee to ask the Agency to look at the issue. The problem with getting more definitive data is that, in the absence of a standard, human exposure to sulfuric acid is not monitored and there is difficulty in obtaining epidemiological data. A method is needed for measuring acid aerosol. More health research is also needed, but there is enough cause for concern about health not to wait any longer. Additional monitoring, laboratory, and epidemiological research should begin soon to answer the question more definitively.

At the end of a major review of a criteria document or issues paper, CASAC has typically prepared research recommendations for the Agency. On the basis of its thorough data review, CASAC makes recommendations to clarify the issues further. For the substantial questions that remain to be answered for ozone and acid aerosols, several years of research are required to address the issues. The subcommittee on measurements did make a specific first recommendation to use the mechanism of an expert workshop to obtain some agreement of the scientific community on what should be measured.

Lippmann offered his view that what should be measured is the free hydrogen content of the particle. No set of data proves that nothing else is present, but the weight of the evidence suggests measurement of the hydrogen ion of the particle. Ammonium bisulfate has the same effect as sulfuric acid at slightly less than half the potency. Ammonium sulfate in most cases is inert. Nitric acid and hydrochloric acid conceivably could have the same effects, but they are vapors except in fogs. Vapors, which are highly water soluble, do not penetrate to the parts of the lung where the effects that have been discussed are produced. So, even though they are equally potent on a filter paper in reacting with basic material, they are not the same in terms of health effects.

The next question to consider at this workshop is how to characterize the acid exposure. The data are fairly consistent with cumulative effects. Dr. John Spengler presented a paper last year that reported that the various summer camp epidemiology studies and laboratory studies showed effects when one accumulated the product of C x T over short periods (hours to weeks). Because these data suggest that the effects are related to a chronic (in the sense of a condition that persists) progression related to cumulative exposure, it is not clear that continuous monitoring is needed to look at short-term peaks. Time resolution is necessary but a daily or multihour measurement should be adequate. Daily average concentrations and seasonal or annual average concentrations are likely to be the most important health-related parameters.

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SECTION 5

THE USE OF MEASUREMENT, EXPOSURE, AND HEALTH EFFECTS DATA IN ASSESSING HEALTH RISKS

Mr. Scott Lounsbury with EPA's Office of Air Quality Planning and Standards (OAQPS) discussed the use of measurement, exposure, and health effects data in assessing health risks and put into perspective the importance of measurement. He gave a quick overview of the process of setting a NAAQS and some of the main factors considered when selecting standards. He discussed the process in terms of health risk characterization and, within that framework, the specific role of measurement in health risk characterization, and focused on acid aerosol measurement issues and needs within the regulatory context.

A simplified overview of the standard setting process was given. First, the scientific community provides a range of information including atmospheric chemistry, methods, sources, exposures, environmental fate, and health and welfare effects. Next, ECAO produces a criteria document that is a comprehensive review and assessment of this information and is essentially the scientific basis for standards. Then, OAQPS produces a staff paper based on the criteria document that interprets the key studies and identifies the important conclusions and uncertainties in the information and is essentially the basis for policy decisions. Toward the end of the process, various regulatory decisions are made leading ultimately to proposal and promulgation of standards.

Setting standards requires good scientific information to make several key determinations. Among the factors to be considered in setting standards are:

- appropriate indicator (and its associated valid measurement methodology),
- averaging time and form of the standard, and
- level of the standard.

Lounsbury then discussed the key components of a generalized health risk characterization. The key components of a risk assessment are a toxicity assessment and an exposure assessment. The toxicity assessment includes input from epidemiological, clinical, and toxicological studies as well as other information about sensitive populations or interactions with other pollutants (e.g., interaction with ozone on health effects end points). For acid aerosols, the epidemiology is based largely on sulfate data, studies where acid data were measured later, or studies where there was a good reason to believe that acid may well have played a role. The clinical and toxicological studies have largely focused on sulfuric acid. The exposure assessment includes a variety of characterization information concerning such factors as sources, indoor/outdoor exposures, spatial and temperature patterns, and other environmental factors. From these two assessments of toxicity and exposure comes an overall risk characterization ultimately leading to regulatory decisions.

Lounsbury emphasized that measurement and exposure data are the foundation of the overall risk characterization process that ultimately leads to good decisions. The exposure assessment part of risk characterization can be no better than the measurement inputs into the process. It is also an interactive process, especially for a pollutant like acid aerosol where information is still emerging rapidly. Measurement provides most of the key inputs into the exposure assessment: concentration, spatial and temporal patterns, etc. Measurement provides exposure information for epidemiological studies directly, but it also plays a key indirect role, because what is learned from characterization may be critical in interpreting epidemiological studies. The characterization information shapes and directs the design of clinical and toxicological studies; e.g., concentrations used, time of exposure, important mixtures of pollutants, and the sequence of the various pollutants in the mixtures. There is also feedback from both of these areas. For example, as the characterization becomes more refined, it can provide feedback for improving measurements because it may show what is adequate time resolution. Does a 24-hour average give a good picture of the exposure or is it more important to have more short-term or continuous monitoring? Health effects information also provides feedback. Morton Lippmann added that as better information is obtained on the critical C x T relationships, focus can begin on better measurement approaches. In the case of acid aerosols, the health effects information also provides feedback on what are the species of concern. For example, should just the strong acid, sulfuric acid, or the whole range of ambient acids (weak and strong) be examined?

Lounsbury then discussed acid aerosol measurement issues and needs. First, health effects data have raised concerns about acid aerosols, specifically on consistency of effects. Several studies are under way or planned, including major epidemiological studies. Standardized benchmarks and standardized data are needed soon to use and interpret the study results later. The biggest limiting factor is probably exposure data including spatial relationships, the nature of peak exposures, and long-term exposures. In addition, the data that are available are limited to some degree by inconsistency and uncertainty in the methods. For example, the historical data very likely have artifact problems, and neither the direction nor magnitude of the artifact are clear. For the more recent data, the methods and controls are clearly better. However, without some notion of intercomparability, the available data are of limited usefulness. It is important to determine the range of exposures and to make the critical links to the health effects information that we do have. The challenge is to effectively join both health and exposure data; the common thread is clearly standardized comparable data from measurement.

For acid aerosols, CASAC has focused on acid particles because they felt that the information in this area was far stronger. CASAC has proposed total titratable acidity as a possible indicator. There are several possible indicators that were discussed briefly in the acid aerosols issue paper. Although it would be useful to have information on all species, that is probably impractical. For most purposes, CASAC felt that total titratable acid would be a reasonable compromise at this point. The health effects information does show that, in general, the effects are related to the strength of the acidity. However, the health effects information is not well enough developed to make final decisions about what species or what cutoff are of concern. In the end, a simple pH strong acid-type measure may be sufficient for a reference method.

Some measurement needs of risk assessment, health research, and models include better information on seasonal, daily, and hourly patterns of acid aerosols; a better sense of the nature and magnitude of peaks and the long-term exposures; better understanding of the spatial patterns of acid aerosols; a good knowledge of exposure both indoors and outdoors (because there is good evidence for high levels of acid aerosols indoors especially with kerosene heaters); and, finally, information on the role of modifiers such as ammonia and other species.

Health risk characterization and regulatory decisions do rely heavily on measurement. Measurement both shapes and is shaped by the process. To make sound exposure and toxicity assessments for acid aerosols requires a range of input from measurements. Standardized comparable measurement data are the critical factor driving the whole process.

DISCUSSION

Dr. Peter Mueller raised a question about terminology, whether acid aerosols meant acid particles or included vapors. Lounsbury stated that although acid aerosols could include acid gases, CASAC focused on acid particles deliberately.

Dr. William Pierson asked how we know that the sulfuric acid delivered actually reaches the lung. Lounsbury said that was a critical question to which we do not have a definitive answer. Morton Lippmann added that there is endogenous ammonia that will neutralize acid before the droplet gets to the lung surface. However, equilibrium is not reached so that only a partial neutralization occurs; the degree of neutralization may vary by individual or by species. Although no measurement technique has been developed for probing deeply into the lungs, logic says that some acid must be delivered to the lungs because effects are seen. William Wilson noted that EPA plans to study the neutralization rate of sulfuric acid by ammonia, particularly ambient sulfuric acid (which has an organic film that could impede the neutralization compared to laboratory-generated acid). Mr. Robert Stevens noted that samples from urban areas have mostly acid sulfate; for these samples, the first hydrogen ion may be neutralized quickly, but the second hydrogen ion is much more resistant when titrated.

SECTION 6

OVERVIEW OF CURRENT ACID AEROSOL MEASUREMENT PROGRAMS

HARVARD SCHOOL OF PUBLIC HEALTH

Dr. John Spengler summarized the scope and the intent of the Harvard School of Public Health's monitoring for acid aerosols and acid vapors. This monitoring serves two purposes: (1) to provide exposure assessments as part of ongoing epidemiological studies in North America, and (2) to develop the science. Harvard's acid monitoring has focused on the following six areas: (1) annual concentrations and distributions of 24-hour acidic aerosols and vapors, (2) continuous monitoring of particle sulfur and acidic species, (3) spatial distribution of acidic aerosols, (4) diurnal variation of acidic aerosols and vapors, (5) indoor acid concentrations, and (6) personal exposures. The Harvard scientists are trying to instigate a routine field method but also to have enough concomitant measurements of meteorological phenomena, aerosols and their elemental composition, and trajectory analyses to increase understanding about the composition and the sources that lead to acid formation.

They have examined ambient concentrations and have tried to characterize annual concentrations and distributions. They have largely limited themselves to a 24-hour measurement, although they have sometimes broken this into shorter time frames to characterize acid aerosols and vapors. They have made a distinct attempt to understand a new vapor component--the nitric and nitrous acid component. Although this may not be as critical as the aerosol component, its significance is important to understand for exposure.

In the past, continuous monitoring was performed for particulate sulfur. The equivalent of 10 city-year's worth of hourly particulate sulfate data was obtained using an instrument that could differentiate the unneutralized from the neutralized fraction. These data can now be matched to clinical studies requiring short time resolutions. Spatial variations have been examined, especially concerning siting. Examinations have been made of how to represent exposures in a community using an ambient monitor at a fixed location. These examinations include studies of diurnal variations of day/night regimes, indoor concentrations of acid, and personal exposures.

Judith Graham's diagram showing effects for clinical studies in the range of 1,000 to 50,000 nmol delivered was interesting because studies by Harvard and others show that children who are outdoors in the daytime can, with even a little exercise, exceed 1,000 to 10,000 nmol delivered over a few hours of exposure. Clearly, the atmosphere is providing exposures of the same magnitude at which chamber studies show effects.

Enhancement of the instruments used in these studies has continued. The device used to characterize the acidity in Harvard's original six cities study measured strong acid levels and had only an ammonia denuder and an aerosol (particulate matter $\leq$ 2.5 μm, PM-2.5) impactor. An ammonia denuder was located in a top compartment, and air was accelerated through two impactor jets. Materials were collected on a Teflon filter with a 4 liters per minute (lpm) flow rate, and pH was measured using a hydrogen ion-selective electrode. This device had a lower limit of detection for a 24-hour sample of about 0.5 $\mu g/m^3$ as sulfuric acid. This is a reasonably correct measurement of the particle acidity, although it underestimates the true acidity because of reactions that can occur on the filters.

Acid aerosol and acid vapor denuder systems will be discussed later by Dr. Petros Koutrakis. These systems have been modified, put in a small-sized unit with portable pumps (4 lpm), and used to determine personal exposures in a few controlled studies done last summer. This work will be continued.

Many of these measurements are taken to coincide with an ongoing, cross-sectional study examining acute health effects of acid exposure, ozone exposure, and exposure to other pollutants. Using a series of 24-hour measurements, the annual and seasonal concentrations of acid aerosols and vapors in some 24 communities are being characterized. About eight cities a year are examined. Approximately 700 fourth and fifth graders in these communities answer a questionnaire administered in October; then a field team performs pulmonary function tests. The acid measurements (24-hour acid) are taken every other day with the denuder system. Measurements of ammonia, sulfur dioxide, ozone, and particulate (particulate matter $\leq$ 10 μm, [PM-10] and PM-2.5) are also obtained.

Eight cities are currently involved in the first round of this cross-sectional health study. Communities were chosen that had an approximate population of 10,000 to 20,000, but were outside of major metropolitan areas (to reduce the complexity of exposures, to avoid the high sulfur dioxide and nitrogen dioxide levels of urban areas, and to include rural areas). High-exposure areas are being contrasted with cleaner sites. For example, the Monterey Peninsula, CA, area (which has clean air) is being considered for contrast with the Livermore, CA, area. For the current sites, nearly a full year's data (taken every other day) have been obtained. Consequently, a considerable data base is being developed to characterize the seasonal patterns and the fractional contributions of the acid aerosol and vapor fractions in these communities. Intercomparison studies have involved the Electric Power Research Institute (EPRI) Operational Evaluation Network (OEN) site at Zanesville, OH, the EPA ME-35 site at Parsons, WV, and the Canadian Atmospheric Environment Service (AES) site at Egbert, Ontario. For these studies, the Harvard denuder system was compared to the filter packs.

Diurnal variations were studied this summer in some of the communities using day/night sampling for 12 hours to look at the different contributions in these communities. Spatial variations are being studied more intensively at two locations (Kanawha Valley, WV, and Newton, CT) where series of monitors have been deployed. Five additional monitors around a central site are being used to understand spatial scales of variation and how to characterize community exposures using a single location.

Recently, indoor measurements were taken in a home built for the Gas Research Institute to test vented and unvented appliances and to look at potential acid formation from emissions indoors. Personal monitoring is also being conducted to look at those activities that either mitigate or yield acid exposures and to compare personal exposures with those derived from measurements at a central site.

Spengler also discussed Harvard's summer acid aerosol studies. The objectives of the set of measurements done in the summer of 1988 were threefold: (1) to determine typical exposures in preparation for locating community health studies, (2) to examine diurnal variations, and (3) to compare Harvard's measurement methodology with that of others. The summer aerosol study involved measurement periods of approximately 20 days at Parsons, WV, Zanesville, OH, and Egbert, Ontario. At Egbert, the equipment was left with the AES to be run for another period of approximately 20 days while another sampler was operated concurrently at Leamington, Ontario; this provided a greater spatial scale to assess the variation of daily acid measurements.

The following comparisons should be obtained using the Harvard annular denuder system (ADS): a 21-day comparison with the EPRI network site at Zanesville, OH, using a transition flow reactor and an open-face filter pack; a 21-day comparison examining EPA's ME-35 network site at Parsons, WV; and a 40-day comparison with the Canadian sites, examining filter packs both with and without spacers. Hopefully, a data base of approximately 80 days of measurements with these different systems will assist EPA in formulating its intercomparison studies.

ROBERT WOOD JOHNSON MEDICAL SCHOOL

Dr. Paul Lioy reviewed the studies being conducted at Robert Wood Johnson Medical School and the Environmental and Occupational Health Science Institute on acid aerosols. The school is trying to develop an integrated program of laboratory and field studies to examine the relationship between microenvironmental and personal exposures to acid particulate species and inhalation health effects. The focus will be on acid particle species because of the potential health effects until toxicological information on species like nitric acid show them to be of concern too.

At present, it is difficult to decide where high acid particle concentrations are likely to occur outdoors let alone indoors since so little information is available. Lioy said that John Spengler has done a magnificent job in the Harvard multicity study in trying to answer some of these questions. The R.W. Johnson group has used a different approach by going to areas both inside and outside the United States that should have acid species in the atmospheric environment.

Lioy specified five objectives of the school's program:

1. Improve and develop laboratory techniques and field samplers.
2. Conduct collaborative quality assurance studies.
3. Design and conduct personal and outdoor human exposure studies for a variety of source-receptor situations.

4. Conduct and/or collaborate in exposure health-effects epidemiological studies.

5. Examine the role of ammonia in breath neutralization of acidity.

The ADS is used now for most studies and the strong acid hydrogen ion is the indicator used for particulate acid species. Modifications to the ADS have been made to make the field samplers more rugged.

The personal and outdoor human exposure studies are specifically designed to evaluate the range of acid concentrations, although it is difficult to determine where the high acids levels are going to occur. In the United States, summertime incidents or episodes appear to be the most likely situations for high exposures to acid aerosols. However, other opportunities for wintertime accumulation should be and are being investigated.

Because epidemiological studies are very difficult to design, the ADS system has been added to ongoing investigations that measure many atmospheric species other than acid aerosols to try to answer the question of whether acid aerosols contribute to the exposure and are a potential health threat. Recently, epidemiological studies to look at high level acid aerosol locations in China and Germany have had designs initiated.

To examine the role of breath ammonia, laboratory-based studies (and eventually population-based studies) are being designed to determine the distribution of endogenous ammonia in human breath and to look at the neutralization capacity of human breath in terms of the actual quantity of acid that would be neutralized upon inhalation into the lungs and then exhalation.

Other studies are being undertaken to look at acid aerosol species in various locations around the world. A study was started in the Netherlands in 1987 for two reasons: (1) to tie into an ongoing investigation looking at the health status of individuals in two communities for over 15 years; and (2) the possibility that part of the regional difference in observed effects (where more effects were apparent in the rural area than in the urban area) might, in fact, be due to acid aerosol, ozone, or a whole complex of pollutants that could be part of this process. The ammonia budget could be examined because the Netherlands has a lot of dairy farming that produces a significant amount of ammonia and may create one of the worst possible cases for nonurban neutralization of acidic species. In addition, high concentrations of sulfur dioxide can travel from locations in West Germany (Dusseldorf and the Ruhr Valley) toward the Netherlands so that, depending upon the amount of neutralization that occurs, either high concentrations of acidic species or totally neutralized aerosol result.

This past year, the R.W. Johnson group participated in a wintertime acute study for acid aerosols in an urban area near Dusseldorf. This location has high sulfuric oxide with episodic conditions associated primarily with wintertime aerosol production. Health measurements and questionnaire development have occurred in the epidemiological component and researchers look forward to seeing some interesting data over the course of the next 2 years.

Another study is under way in China to look at the health effects of air pollution on lung function of children in four cities with different and extremely interesting environments. One city, Guangzhou, is in the lower tier of China and probably has very little coal burning (except for cooking) but may have high ozone. Another city, Wuhan, was the location of an intensive study this past winter. Wuhan looks like the London of smog infamy in 1952. The study will be a longitudinal study taking acid measurements and other pollutant measurements over the course of 3 to 5 years and taking semiannual lung function measures on children in these cities. The location is a small, 1-km block containing about a thousand children with one outdoor air monitor and indoor monitoring. The children and the monitoring all are within this location and there is very little movement of people, so one has a tightly contained population to study exposure and possible effects.

Different routines have been used to measure acid because no standard methodology has been developed for determining what periods of time to measure. Researchers face a situation of looking at both chemical characterization and exposure. A balance needs to be struck between understanding the nature of acid aerosol chemistry now and what will ultimately be needed for epidemiological studies, chronic vs. acute effects. Among the sampling regimes that have been used are: 24 hours in the Netherlands, 24 hours (and some 12-hour studies) in New Jersey, 24 hours in West Germany, and 8 hours in China. For Wuhan, China, a modified technique is used in which the ADS is turned on for 15 minutes every 2 hours over 7 days and then the sample is collected. Three denuder systems are used on top of the sampler to prevent loss of material from the filters. However, laboratory experiments are being conducted to ensure that this approach is useful.

ENVIRONMENT CANADA

Dr. Al Wiebe described the major measurement programs for atmospheric particles that the Canadian Atmospheric Environment Service (AES) has undertaken. They are the Canadian Precipitation Monitoring Network (CAPMoN) air filter network, field studies of acid precipitation processes using specially instrumented aircraft, and, as a subcomponent of some of these studies, the chemical and physical characterization of the atmospheric particles to obtain size distributions, masses, and chemical composition in various size ranges.

The objectives of the CAPMoN air filter network are to:

1. measure regional-scale spatial and temporal variations and long-term trends in the chemical composition of air and dry deposition in Canada,

2. provide a data base for use in the verification of long-range transport models,

3. provide data for chemical process studies, and

4. provide a set of standard methodologies for use in all regions of Canada to ensure compatibility with other measurement agencies and networks.

The sampler used is the Canadian filter pack, a simple device consisting of three stages with an air flow of approximately 15 lpm. The atmospheric particles are collected on the first-stage Teflon filter. With the advent of nitric acid measurements (beginning in 1982), a second-stage nylon filter was inserted for the collection of nitric acid. Finally, the back filter is a Whatman 41 filter impregnated with potassium carbonate or citric acid for the collection of gaseous sulfur dioxide or ammonia. Typically, eight of these filter packs are deployed in the field for obtaining 24-hour samples during a week. The aerosol filter, even though it only collects one sample for a 24-hour period, is exposed to the ambient atmosphere during the week. Thus, neutralization of ammonia could be a very important feature. The filters are put in bags and sent back to the central laboratory for analysis of the common inorganic constituents of concern in acid rain issues.

The earliest air monitoring station began operation in 1977 at Chalk River and provides a data record that goes back about 12 years. The newest station is at Egbert. Several of these sites are located in an area called the calibrated watershed. The data generated are used for estimates of atmospheric dry deposition to the watershed for mass balance studies.

Wiebe discussed the artifact collection of nitric acid on the second filter by the possible evaporation of ammonium nitrate from the particle filter. The AES has participated in three separate intercomparison studies using the filter pack. Two of these studies were done in California. One was for about a week in August 1986 during which the AES operated two systems: the filter pack and a tunable diode laser supposedly free of artifact interferences. In general, the uncertainty due to the volatilization has not been shown to be any worse than 20% in any of the intercomparison studies.

ELECTRIC POWER RESEARCH INSTITUTE

Health Research

Dr. Ronald Wyzga discussed the recent results of EPRI's health research and its implications for the workshop participants in their task. He emphasized the need to be as flexible as possible because there are significant uncertainties in the health area.

The first issue discussed was identification of the agent of concern. There are theoretical reasons that have led people to look at the hydrogen ion. A lot of evidence exists that is consistent with the hypothesis that the hydrogen ion is the agent of concern. However, not all evidence is consistent with that hypothesis. Most of the work to date has been done on sulfuric acid. One of the end points of greatest concern (as mentioned by previous speakers) was clearance studies. An experiment using sulfuric acid and ammonium bisulfate was conducted to see how the results for alveolar clearance compared. If there was exact equivalence of hydrogen ions, sulfuric acid would be approximately twice as potent as ammonium bisulfate. In the experiment, the results did not support this hypothesis. The expected rate of changes in clearance was calculated for ammonium bisulfate based on the sulfuric acid results. The observed rates of changes in alveolar clearance in rabbits for ammonium bisulfate were much lower than expected. Three explanations were given for these results. One, there could be some difference in the rate of dissociation of the hydrogen ion for these two compounds. Two, differential rates in terms of neutralization might exist for these two aerosols. Third, and perhaps most likely, there may be differences in the hygroscopic properties of these two aerosols that could affect the particle size distribution and also the distribution of the aerosols within the lung. This indicates how important it is to consider the size of the aerosol in measurements. In some experiments with beagle dogs, a larger diameter aerosol seemed to elicit responses more readily than some of the smaller diameter aerosols.

The system used to measure acid aerosols should be consistent with the type of measurements that are undertaken for other pollutants. There is some evidence that there may be synergistic responses. Some recent studies were done at the University of California at Irvine (UC-Irvine) to look at the rate of killing of lung cells in rats. Several different atmospheres were investigated (clean air, sulfuric acid, ozone, and sulfuric acid plus ozone). No change was observed when comparing sulfuric acid alone to clean air. When the rats were exposed for 4 hours to ozone, the rate of cell killing almost doubled. When the rats were exposed simultaneously to a very high level of ozone with sulfuric acid, the rate of cell killing approximately tripled indicating an apparent synergistic effect. Copollutants should be measured because some of the most sensitive end points that may be examined may involve coexposure to such pollutants. Time scale also needs to be considered. The suggestion has been made that if the experiment were redesigned, the peaks should be adjusted so that the peak of ozone occurs before the acid aerosol (instead of simultaneously) because peaks of ozone exposure tend to occur a little before peaks in acid exposure. If true, it is noteworthy and something that could be incorporated in future experiments.

For some end points such as clearance, evidence exists that is consistent with the hypothesis that total exposure is significant. However, that is not true for all end points. If all turnover end points are evaluated, there is increased response after 4 hours of exposure for 1 day, but after 5 days there was no response for any of the enhanced environments. This suggests that it is acute exposure that is more significant for this particular end point. For yet another end point, research at Rancho Los Amigos on a large group of exercising adolescent asthmatics who were exposed to sulfuric acid for periods of 10 minutes indicates that a subset of these asthmatics may be sensitive. However, the key factor as health research progresses is that for some end points, short or peak exposures must be considered and it is not known which type of exposure may yield the most appropriate end point.

Wyzga highlighted four issues that he believes should be considered in developing different measurement techniques. First, there is uncertainty about what the correct agent is. Is it the hydrogen ion or some modification? Basically, contributions of hydrogen ion from acid gases are treated differently than those from acid aerosols. Can one assume that all hydrogen ions are equivalent? Because the information is equivocal, any method should provide sufficient flexibility. Second, size and the hygroscopic properties of the various aerosols must be considered. Third, is the issue of time and short- vs. long-term exposures. For some end points, total or long-term exposure may be the correct measurement; for others it appears to be short-term. Thus, the capability of having both must also be considered. Fourth, copollutants also need to be evaluated; ozone and nitrogen dioxide have been mentioned. Morton Lippmann referred to a study that found that the absorption of acid aerosols on fine zinc oxide particles apparently made them more available. If that is the case, it is very important to look at the simultaneous exposure to copollutants.

In conclusion, Wyzga described the research program that examines some of these issues during the next 2 years. This includes work at NYU to investigate the hydrogen ion hypothesis fully. By looking at a whole range of dose levels, including some very low ones (most animal experiments have been done at 100 $\mu g/m^3$ or higher), some measure should be obtained of how much may be getting into the lungs to determine if any neutralization is occurring at relatively low doses. An investigation of the C x T or total dose phenomena is also under way. The results to date are more or less consistent with that hypothesis, but it is unclear how that hypothesis stands up at relatively low concentrations. Also, the results to date have had a very high correlation between the C x T measure and the concentration measure, and it has been very difficult to discriminate between the two as to which association is more important. Also under way at UC-Irvine are studies on mixtures (including different particles, ozone, nitrogen dioxide, and sulfur dioxide). Wyzga cautioned that it is important that to keep an open mind and be flexible.

Atmospheric Research

Dr. Peter Mueller noted that, in contrast to a very deliberate and well-organized research program to investigate the effects of inhalation of acidic aerosol, EPRI currently does not have a program to investigate the acid aerosol question specifically from the point of view of the chemical and physical sciences. EPRI has been looking at the atmospheric aerosol for a variety of reasons and has undertaken projects that provide answers to aspects of the acid aerosol issue, although they are not deliberately geared to answer the questions raised by this workshop.

One of the difficulties in looking at atmospheric particles and aerosols is that some of the constituents are continuously in transition between the gas and the particle phases. The question raised is how to obtain accurate measurements for sulfuric acid, ammonium sulfate, or ammonium nitrate for example when, at the very step of taking the sample and moving the material to a different environment for laboratory analysis, the sample is altered. At the moment, there is no measure for the degree of adulteration of the sample. Thus, shootouts and field method intercomparisons will not provide evidence to prove which method is actually right. If accuracy is desired, a methods intercomparison should not be the first priority. The next step ought to be to understand the stability of the aerosol over time so that the extent of adulterating the aerosol can be determined for various sampling times.

There is evidence that after sampling for a few hours, the aerosol has been altered, depending upon how the sampling was done. Trying to work around the problem by using either ADSs or filter packs in an effort to separate the gas phase from the particle phase in the act of sampling is really inappropriate, because in the act of separating with denuders, the equilibrium between the particle and gas phases is changed. To add another piece of equipment to account for phase differences and make a correction compounds the problem. EPRI conducted studies to see how much of a problem really existed and what kinds of uncertainties could be accommodated. Sampling with imperfect instruments is needed to obtain some idea of the ranges involved for the quantities of interest. This information can then be used to decide the accuracy goal. This is the basis for establishing data quality objectives.

Mueller briefly mentioned some of the studies EPRI has conducted. One cooperative study with the Canadians and EPA is being done in the eastern United States to measure the chemistry of the precipitation, particulate matter, and several gases, using filter packs and other instruments. There are three or four locations where collocated sampling is being performed, both duplicate sampling by a single participant and duplicate sampling by coparticipants. However, the initial data from the filter packs show some large deviations, even for duplicate sampling with analysis performed by the same laboratory, even for sulfate. Uncertainties and imprecision stem from a host of variables, which are not necessarily related to the fundamentals of the measurement technology itself, and are more related to practical matters associated with quality control, such as handling the materials, keeping track of flows, not mixing up filters, not having leaks, etc. It is absolutely essential to have quality control tests as part of the standard operating procedures.

Nonetheless, the accuracy of the methodology is still a problem that may only be solved by making short-term measurements. For very low concentrations, this means sampling periods of about 1 second to 1 minute or so in duration. Two patents have recently been granted for probes that can be put inside the samplers to find out what really is happening, compared to the hypotheses of what is happening. Also, measurements can be made in the actual environment, integrated, and compared to averaged samples taken. A benchtop version for this method, called frequency modulation (FM) modulation spectroscopy, is now available. It can determine many gases (especially ammonia, sulfur dioxide, nitrogen dioxide, and ozone) at the parts per trillion concentration level in a minute or less.

The substantial uncertainties in the measurements from field sampling filters can be illustrated by examining the results of an instrument used in the SCENES program. This instrument inlet has a PM-15 cut; the air is sucked through a duct into a shelter; cyclones are located inside the duct to obtain PM-2.5. Initially, samples were obtained using an open-faced filter and the material analyzed for mass and sulfate. For the last few years, the Teflon filter was not analyzed for ammonium and nitrate because the distribution did not appear to make sense. A denuder system was devised for the high flow rates, with Teflon and impregnated filters following it, to try to account for the disequilibrium created. Gas-phase particulate nitrate on the nylon filter preceded by a denuder is large compared to the nitrate obtained from a filter not preceded by a denuder. If the nitrate filter is preceded by a denuder and followed by a back filter, the sum of what is on the front filter, plus the back filter, is roughly twice that obtained with just an open-faced Teflon filter. An error on the order of a factor of two can be important. Obtaining the real nitrate concentrations under circumstances where particulate nitrate concentrations exceed 1 $\mu g/m^3$ is important enough to use denuder sampling at one sampling location (Meteor Crater, AZ) to investigate the phenomenology. Mueller concluded that it is acceptable to sample with imperfect methods to obtain an idea of the range of the pollutants of interest and to use that information to decide goals for accuracy.

CALIFORNIA AIR RESOURCES BOARD (CARB)

Dr. Doug Lawson discussed three studies that CARB has conducted in the past 3 years: the nitric acid shootout in 1985, the carbon shootout in 1986, and the Southern California Air Quality Study (SCAQS) in 1987. He also discussed briefly the atmospheric acidity research program that CARB is undertaking. First, Lawson discussed the nitric acid shootout that was done at Claremont. He disagreed with Peter Mueller's comments about shootouts, noting that they can provide useful information if done properly. However, there are too many that are done without appropriate references and do not yield much information. He also noted that he disagreed with John Spengler's comments on collaborative quality assurance and stated there is no such thing as collaborative quality assurance, because one must have an independent party do that.

The objective of the nitric acid shootout was to evaluate sampling methods for nitrogenous species that would be used in the 1987 SCAQS. Twenty groups from the United States, Canada, and Italy were involved in the study. The results of the study were presented in the August 1988 issue of Atmospheric Environment (Hering et al., 1988).

In 1986, CARB conducted the carbon shootout, which included 30 groups. The objectives of the carbon shootout were to:

- Compare sampling methods and analytical techniques (for total, organic, and nonvolatile) aerosol carbon.
- Assess sampling methodologies for accuracy and precision of various species, including formaldehyde, hydrogen peroxide, and nitric acid.
- Obtain data on speciation of as many gas- and particle-phase carbonaceous species as possible, in order to assess the relative importance of these species in a polluted atmosphere.

The funding of SCAQS a year ago was about $10 million. It has increased about $2 million over the last year as the data are being analyzed. The overall objective of SCAQS was to develop a properly archived data base for use in development and validation of air quality simulation models (for ozone and PM-10 especially), to understand the relationship between nonmethane hydrocarbons and nitrogen oxides and ozone, and also to look at other components, such as atmospheric acidity and visibility.

SCAQS consisted of nine sites throughout the South Coast Air Basin. Measurements were made in the summer of 1987 at nine sites and six sites in the fall. Fifty different research groups were involved with the program. Currently, data are being received from the groups. The measurements at the nine sites in the basin included the following routine measurements: meteorology (wind speed and direction, temperature, dew point, and ultraviolet radiation), gases (ozone, nitric oxide, nitrogen dioxide, and nitrogen oxides) and particles (PM-10, mass, sulfate, and nitrate). Other measurements that could be considered contributors to acidity include: nitrogen oxides, ammonia, nitric acid, hydrogen peroxide, particulate sulfate, nitrate, and ammonium ion in both PM-2.5 and PM-10 as well as size-resolved measurements of components such as sulfate, nitrate, hydrogen ion, and ammonium ion. About $600,000 will be spent for the data analysis this year.

Lawson agreed with Ron Wyzga that one must look at copollutants to understand what is occurring. Looking at hourly averaged data from the carbon shootout, there is a very good correlation between ozone and nitric acid, and both peak at exactly the same time. He emphasized that CARB is looking at atmospheric acidity, not just the particle acidity. CARB also wants to look at copollutants since many of these peak at about the same time, though some at different times of the day.

Lawson emphasized one should not look only at aerosol acidity. Data from the carbon shootout showed that the major contributor to acidity in Los Angeles was nitric acid and the close association of nitric acid with ozone could mean that any urban location in the United States with high ozone might also have high nitric acid. Also, if the contribution of gas-phase organic acids such as formic and acetic acids is evaluated, it is found that they contribute significantly to total gas-phase acidity. Other gaseous acid species measured included nitrous acid and hydrochloric acid.

Lawson emphasized that health effects studies should be done in an urban area because of the population concentration and to do this total acidity and not just aerosol or particle acidity must be evaluated. There is a lot of organic acid in Los Angeles and it should occur in any urban area that has hydrocarbons. During the carbon shootout, the maximum particle sulfate that was measured was about 11 $\mu g/m^3$; even if the sulfate in Los Angeles were all sulfuric acid, it would be a relatively small contributor to total acidity.

Health effects researchers should be consulted to understand what types of averaging times are needed. With shorter averaging periods, great differences in concentrations are seen between shorter and longer averaging times. Looking at preliminary data for ozone from the carbon shootout, the maximum concentration for a short sampling period is 0.3 ppm, while for 24 hours it is 0.08 ppm, roughly a factor of four. Similarly, a factor of roughly four for nitric acid is obtained in the change from 5-minute to 24-hour averaging times. It needs to be determined which averaging time is appropriate for health effects work.

Discussion

Morton Lippmann noted that the workshop may be taking a sidetrack. The purpose of the workshop is to assist in standardizing methods to measure an atmospheric entity that has been associated with health effects in laboratory, clinical, and epidemiological studies. That entity is associated with particle acidity. He could understand the scientific interest in total acidity, but vapor acidity is a different entity with different potential effects on the respiratory tract, primarily the upper respiratory tract. It is important to realize that EPA needs help in looking at a particular entity in the atmosphere that has associated health effects and to have standardized monitoring methods to be able to measure it.

Lawson responded that Lippmann's point was well taken and that he did not have an argument with it. He added that given the expense of doing an acid aerosol study, it pays to look at additional pollutants. This type of study is not done very often and, in doing it, a much higher contribution to total acidity can be seen from the gas rather than the particle phase. Lippmann disagreed again.

BROOKHAVEN NATIONAL LABORATORY (BNL)

Dr. Leonard Newman noted that a successful intercomparison could be done by comparing how one selected method was used by different investigators. However, if a shootout is defined as groups of people going out and making measurements by whatever method they want to select, then it is not possible to decide which is the best method as a result of those measurements. Even if measurement results by two methods agree and from a third method disagree, that does not mean that the results of the two methods agree for the correct reasons. Until there is a true reference, i.e., a method of saying what the sulfate aerosol is or the acidity in the air really is, one cannot have an appropriate shootout.

To elaborate on this idea, Newman quoted from a 1976 paper entitled "Validation of Methods for Determination and Speciation of Sulfate Aerosols" (Schwartz and Tanner).

> Because of the recognition of the differential environmental and health impacts associated with aerosol sulfuric acid and its ammonium salts, there is urgent need for validated methods for speciation and determination of these compounds. We propose to conduct an extensive validation study of the scheme for speciation and determination of sulfate aerosol by differential solvent extraction that has been developed in this laboratory. This study will utilize synthetic and ambient aerosols, and will employ both redundant determinations and a variety of carefully designed controls to assure reliability of the speciation scheme.

Although research interests and methodology may have changed, the need for validated methods for speciation and determination of these compounds remains.

Newman offered his views concerning what measurements should be made. For monitoring requirements, first there must be a measure of total sulfate. It is best to determine the composition of sulfate with a minimum of one size cut. However, it may be more desirable to use two size cuts. His filter of choice for sulfate is the quartz filter, to shorten sampling periods using very fast flows (a cubic meter per minute). Also, the quartz filter has a large surface area and there is less likelihood of having interactions between particles as they are collected from one moment to the next. With a quartz filter, by sampling for a period of 10 minutes, enough material can be collected to analyze without any interactions of basic particles with acidic particles. He did not understand why the scientific community has not adopted the quartz filter to a greater extent unless the reason was, in part, that the quartz filter requires pretreatment of the filter to neutralize any basic sites that might be on it. However, if there was greater need for quartz filters for monitoring purposes, the industry might do the neutralization pretreatment.

BNL filter packs use as a second stage sodium chloride-impregnated paper for the collection of nitric acid as opposed to nylon filters. Because of apparent problems associated with trying to measure nitric acid on nylon, the use of sodium chloride-impregnated filters should be considered. The third filter used in the BNL filter pack is the carbonate-impregnated Whatman filter. The method of choice for sulfate analysis is almost universally agreed to be ion chromatography. The method of choice for determining acidity should be the Gran titration, which can be automated and done almost as routinely as can a pH measurement. It provides much more information because the presence of weak acids can be detected by examining the shape of the curves.

For research interests, both the overall acidity and the form of the acidity (i.e., whether sulfuric acid, ammonium bisulfate, or sulfate) must be found and the technology is there to do it. One should be able to do the composition discrimination by particle fraction, i.e., the acidity within a given range of particle size. BNL has developed this capability by using the diffusion sampler technique. BNL also has the ability to measure the chemical composition of particles, particle by particle, using a technique for suspending a submicron aerosol particle in an electrostatic device. By using a laser technique, the Raman scattering of that particle is observed. Looking at the spectra of a single suspended particle of letovicite (which is partially neutralized sulfuric acid), two peaks are observed while another spectra for ammonium bisulfate as a solid particle shows two peaks at different locations. Thus, the identity of the particle can be clearly distinguished and it can be determined whether there is a mixture of both species in a single particle. A spectrum of a bisulfate particle subjected to sufficiently high humidity to get a liquid particle shows that the bisulfate has disassociated to sulfate and acid so that one can see the bisulfate peaks and the sulfate peaks. Thus, bisulfate ions or sulfate ions in a single particle can be differentiated. For these experiments, the particle is generated in the laboratory, suspended in the device, and kept for as long as necessary to measure its composition. However, using this device, it should be possible to sample particles from the atmosphere, pass them through the device, obtain selected spectra, and integrate with time to get the chemical composition of particles with respect to time.

SECTION 7

CURRENT ACID AEROSOL MEASUREMENT TECHNIQUES

HARVARD SCHOOL OF PUBLIC HEALTH

Dr. Petros Koutrakis noted that in 1984 Harvard used a simple device to measure acid aerosols that consisted of a pumping unit, an impactor to collect 2.5-µm particles, and an aluminum honeycomb denuder to remove ammonia during sampling. He showed results using this device taken from two of the six cities Harvard studied. The sulfate results were similar for the two sites and showed that toward summer there were higher sulfate concentrations. However, the acid content of sulfates was completely different in that the first site had much more acidic sulfates than the second site. Thus, it can be concluded that sulfate concentrations should not be used to predict acid aerosol concentrations.

The size distribution of acid aerosols was studied to see how it agreed with the sulfate distribution. A micro-orifice impactor developed by Dr. Virgil Marple was used. The top of the impactor was equipped with ammonia denuders to strip ammonia from the air stream. The study showed that the sulfate was mostly collected at the fourth stage (which had an aerodynamic diameter of 0.4 µm), and the acidity of the particles showed the same size distribution. For particles larger than 1.0 µm, there are some negative values that suggest there is a contribution of alkaline and basic particles that can neutralize part of the acidity. Because of the good correlation between size distribution, aerodynamic diameter, and relative humidity, the size distribution of particulate sulfates can be predicted using the relative humidity, given the number of moles of sulfates per droplet.

After these preliminary studies, more sophisticated systems were felt to be necessary to measure the aerosol acidity. One of the systems that can provide additional information is the ADS. The annular denuder technology was developed in Italy although an inlet was developed by Harvard and EPA to remove coarse particles. The first annular denuder removes sulfur dioxide, and nitric and nitrous acid; the second annular denuder (which is coated with sodium carbonate) collects nitrates and nitrites that can come from artifact reactions of nitrogen oxides or peroxyacetyl nitrate (PAN) inside the denuder; and the third denuder (which is coated with citric acid) traps ammonia and protects the acidic aerosols from ammonia neutralization. After the denuders is a filter pack with four filters. It has a Teflon filter that collects the fine particles that can be used to make measurements of acidity, sulfates, nitrates, nitrites, and ammonium. However, many particles can go into the gaseous phase (e.g., ammonium nitrate), so a second filter (a sodium carbonate-impregnated glass fiber filter) is used to trap all the acid vapors that come from the aerosol phase. The third filter is another sodium carbonate filter again to trap acidic vapors that can be an artifact formed by gases interacting with the filter media. The last filter is a citric acid-coated glass fiber filter that traps basic vapors (such as ammonia).

Koutrakis next gave some examples of artifact problems. Typically, the second filter has lost all vapor-phase nitric acid, leaving particulate nitrates, which can come from the dissociation of ammonium nitrates. Nitric acid can also come from the neutralization of ammonia and sulfuric acid or any other acidic sulfate and ammonium nitrates. The nitric acid will go to the second filter and the ammonium sulfates (a neutral salt) will stay on the Teflon filter. Thus, the acid aerosols can be neutralized by volatile ammonium salts. To test this hypothesis, a laboratory experiment was undertaken in which a nebulizer was used to generate particles. The experiment used two systems and generated different particles. In both cases, there were 3 hours of sampling for each component at room temperature. For some samples, the relative humidity was 70-80%, while for others it was 50-60%. In one case, only ammonium sulfates were generated, passed through the denuders, and collected on the Teflon filter. For the other case, ammonium nitrate was used. In this case, most of the material is collected on the Teflon filter, but about 10% goes to the second filter as nitrate, and an equal number of moles goes to the last filter. When sulfuric acid was generated, most of it was collected on the Teflon filter along with some ammonium. However, when sulfuric acid was first passed for 3 hours and then ammonium nitrate for 3 hours, all sulfates were collected on the Teflon filter, but a substantial amount of acidity did not stay on the Teflon filter. The acidity was neutralized by ammonium nitrate. If the reverse experiment is done where first ammonium nitrate is passed and then sulfuric acid, the situation is worse. This is because, in the beginning, ammonium nitrates are deposited and, after passing sulfuric acid, there is a nonequilibrium situation for the collected ammonium nitrate particles; they disassociate, forming ammonia and nitric acid. The nitric acid will go through because the Teflon filter is acidic and the ammonia will stay and neutralize the acid. Thus, when 900 nmol/m^3 of acidity was deposited, only 300 nmol/m^3 of sulfuric acid was found. About 1300 nmol/m^3 of hydrogen ion is missing; it was neutralized by ammonium nitrate.

These laboratory experiments indicate that other processes are occurring and may require a correction to the apparent acidity measured on the Teflon filter so the total acidity will be equal to the apparent acidity plus the amount that was neutralized. At the beginning of the study, there was some evidence that this kind of process is occurring in the real atmosphere. However, after the first month, there was contamination of the glass fiber filters with ammonia. At Newtown, CT, the apparent acidity was 34 nmol/m^3, and the correction was 86 nmol/m^3.

ROBERT WOOD JOHNSON MEDICAL SCHOOL

Dr. Jed Waldman noted that Doug Lawson had given a very insightful discussion about total acidity and its importance even though it might be considered only a West Coast problem. Atmospheric acidity is not something easily grasped because it moves between phases and can go from one species to another. Thus, the occurrence of nitric acid or other strongly dissociating vapor phase acids can, in fact, influence the amount of strong acidity in the aerosol phase.

Waldman then described the system used by the R.W. Johnson Medical School. The ADS was first developed in Italy and uses the principle that by lowering the Reynolds number one can scavenge out reactive gases to a surface of an annulus while letting the fine particles continue through. The system includes an inlet, which is a preseparator, three annular denuder tubes, and a three-stage filter pack. An elutriator removes the largest particles and is followed by a jet impactor with a size cut of about 2 - 2.5 μm. Then there are three denuders. The first two are coated with base and the third is coated with acid. This is followed by a filter pack that removes the particles. The first denuder tube is coated with sodium carbonate. The acid gases (sulfur dioxide, nitric acid, and nitrous acid) react well with the carbonate-coated walls of the tube. Because nitrogen oxides can create an artifact on that tube, a second sodium carbonate tube is used to correct for that. The third tube is coated with citric acid to remove ammonia. In the filter pack, a Teflon filter removes the aerosol components (sulfate, nitrate, ammonium, and hydrogen ion). However, some combination of volatile components can go past the Teflon filter as nitric acid or ammonium nitrate. The second nylon filter and the third filter, a citric acid-impregnated glass fiber filter, collect certain gaseous species and serve as a means to correct for this.

The level of detectability using the ADS is about 0.2 ppb for the gaseous species (sulfur dioxide, nitric acid, nitrous acid, ammonia) and about 0.5 $\mu g/m^3$ for the aerosol species (sulfate, nitrate, ammonium, and acidity or hydrogen ion). Using sulfate as an example species, that translates to about 10 $nequiv/m^3$ on a 24-hour basis.

These measurements are made in support of health studies. In Wuhan, China, the samplers were placed atop the school and included both ADSs and dichotomous samplers. In addition to the system components, there is a field box for the glassware and the pump. A gas meter is located behind the box to obtain the total flow through the system as well as to calibrate the flow into the inlet before and after sampling for an unambiguous measurement of the amount of gas through the system. Sampling runs lasted 8 hours. The box protects the glassware and keeps it at slightly above ambient temperature to keep condensation from occurring. With enough care, it appears that a complex system can be operated virtually anywhere.

Many different aliquots are used for the analysis. Extracts of the tubes are analyzed either for anions, ammonium, or acidity. Ion chromatography is used for the anions (sulfate, nitrate, and nitrite), a colorimetric method (indophenol method) is used for the ammonium, and an acid addition method is used for pH. In the acid addition method, the Teflon filter is extracted in a dilute solution of strong acid to eliminate the influence of the weak acids (5×10^{-5} M perchloric acid $\rightarrow pH_0 = 4.32$). Then sulfuric acid and perchloric acid standards are used for quantitative acidity determination. Titrations have been done recently. Looking at the summer camp study data, there was about a 10 or 20% excess for total acidity compared to strong acidity using only an end point and not a Gran titration. With computer-aided data acquisition systems, a complete titration should be easy to do and titration should make a comeback.

Waldman noted that quality control (QC) is a big issue as Peter Mueller mentioned. There are many aliquots and much sample handling, and care must be used to keep track of all samples. A mechanistic approach should be instituted to eliminate contamination as much as possible. Thus, portable air scrubbers are used to obtain zero air at all site locations, and blank sets are used. In addition, assembly and disassembly takes place in the laboratory only, and both filter blanks and spiked filters are used. For field measurements, flow measurements are taken at the inlet and gas meters are used to measure total volume.

Waldman briefly discussed some ADS measurement issues. He noted that care must be taken to avoid prerun and postrun contamination because of coated surfaces. There is also the issue of postrun stability of the filters as well as questions about the stability of species on the denuder tubes. For the nitrite artifact correction, data in the Netherlands indicated that nitrite was quite stable in denuder extraction solutions in the winter, but in the summer there is a conversion to nitrate. This may be occurring because ozone or other oxidants pass through the system, but once extracted there is no further oxidation that would confound the correction. Many issues are yet to be resolved including those that Petros Koutrakis mentioned, namely, hydrogen ion stability and neutralization on Teflon filters, or nitrate (nitric acid or ammonium nitrate) loss from Teflon filters. A back-up glass fiber filter impregnated with citric acid is being used and these results may be able to serve as a contrast to corroborate the experiences at Harvard. Finally, there is the issue of what species is being measured and the reason for measuring it. Strong proton or minimal acidity has been used in most studies, but considering the lung itself as a somewhat alkaline object would indicate that, with respect to physiological fluids, most of the components in the atmosphere that are being measured (the weak acids and strong acids) will be titrated by the lungs themselves.

Discussion

Peter Mueller noted that post- and prerun stability and contamination are important issues. To enhance postrun stability, EPRI has decided that all of their network samples will be shipped cold with temperature measured upon arrival at the lab. Waldman responded that, in terms of mass transfer, putting air through a filter will create more rapid changes for a chemical system that is out of equilibrium than a diffusional change. For a filter at any temperature, the quiescent diffusion due to dissociation will be much slower when compared to taking a gas-phase species and passing it through the filter. By the time the sampler is turned off, the damage may, in fact, have been done. Mueller responded that EPRI had seen as much as a 40-60% loss of nitrate between completing a run and analyzing it in the laboratory; he mentioned it because postrun stability will have to be a very important consideration in developing the methods.

NEW YORK UNIVERSITY MEDICAL SCHOOL

Dr. George Thurston described efforts at NYU for monitoring acid aerosols. They have conducted summer camp studies and other short-term studies using dichotomous samplers with denuder inlets (Fairview Lake and Tuxedo, NY, are examples). Acid aerosol measurements have also been taken in Toronto for three summers.

Currently, a year-round project is under way to monitor at sites in New York State. Primarily, fine aerosols (2.5 μm or less) are collected daily and analyzed for strong acidity, sulfates, nitrates, and ammonium. The Harvard sampler with cascade impactor and honeycomb denuder is being used with some modifications developed by Marple, Spengler, and Turner. The samples are sent from the laboratory at NYU and personnel of the New York Department of Environmental Conservation (DEC) handle the samples at the field sites. The samples are out for a week, collected, and then shipped back. The system is designed to be used without constant attention and to use regular employees without extensive specialized training or background. There are three sites (outside of New York City at White Plains, Albany, and Buffalo) that are also used by the DEC to collect routine ambient data such as ozone, sulfur dioxide, nitrogen dioxide, etc. In conjunction with this study, hospital admissions data will be examined. Thus, 24-hour samples are being collected every day throughout the year using a sequential acid aerosol system. The sampler system consists of a sodium carbonate-coated denuder for the nitric acid followed by a citric acid-coated denuder. Impaction plates then remove the larger aerosol and a Teflon filter is followed by a nylon filter to pick up any volatilized nitrates.

Sampling begins on Tuesdays and runs sequentially using an electronic control box with battery backup to switch the solenoids for each sampler on and off at midnight in sequence. There is an elapsed time monitor to tell how long each sample ran. If, for any reason, there is a problem with changing on Tuesday, an extra sampler is available to be used. Usually, this sampler is not used and becomes the field blank. There is also a positive control consisting of a sulfuric acid-doped sample that goes out into the field and returns with the other samples without having air pass through it. The pump uses a mass flow controller that runs continuously at 4 lpm and is switched sequentially during the week. In addition, a flow rate voltage recorder with battery backup continuously monitors the flow rate. Each sampler has quick disconnects so that the field personnel can easily send back the samples via United Parcel Service without handling the samples. The units have been in use about 9 months and are very durable. There is no follow-up citric acid-coated filter, but that could be added.

The objective of the study is to do time series analysis to determine an association between aerosol and morbidity. Cross-sectional studies may also be possible. Sulfate data will be examined to allow a direct test of the hypothesis that acid aerosol is a causal factor in air pollution morbidity associations previously reported.

Discussion

Peter Mueller asked how soon after receipt are samples analyzed. Thurston replied that there had been a delay in analyzing the samples because there had been difficulties setting up the ion chromatograph and getting it to run reliably. In the meantime, the samples are being stored in a dry state inside petri dishes surrounded by citric acid paper. Once the backlog is reduced, the samples should be analyzed quickly.

John Watson asked if the inlets were transported back and forth or remained at the site. Thurston responded that the whole unit goes back. After disconnecting, caps are put on the top and bottom and the units are shipped back sealed. The filters are removed in the laboratory under a hood in an ammonia-free environment.

Peter Mueller asked if there was any collocated sampling. Thurston responded no. Mueller stated that it should be done. Thurston asked if he meant a different unit; Mueller replied that he meant a similar unit sampling at the same time. Thurston said he would discuss this with Mueller and would be glad to set it up if the proper support were available. Mueller replied that he was very serious about the need to do the collocated sampling, and that he would do it, even if it meant reducing the number of sites to two. Petros Koutrakis said that he felt Mueller was overstating the potential for within-site variation and that he could show data with little difference. Not knowing what had occurred at Mueller's sites, he nonetheless would suspect the methods themselves. Koutrakis stated that they had run many collocated samples and never saw more than 5 to 10% difference.

Dr. Walter John asked what would happen if one of the solenoid valves did not close completely when switching to the next one. Thurston replied that there would be flow through both units, but there had not been any problems with the solenoids. They have been monitored, tested, and checked periodically to make sure they are opening and closing. Moreover, the solenoids are in a temperature-controlled environment. However, it is a possibility to look into even if routine checks have not revealed such a problem.

CALIFORNIA AIR AND INDUSTRIAL HYGIENE LAB (AIHL)

Dr. Bruce Appel discussed three general areas: first, a semicontinuous sulfuric acid sulfate monitor, specifically a laboratory evaluation of interference effects as well as field trial results in Southern California; second, the effectiveness of an ammonia denuder for the collection of particulate acidity; and, third, the issue of strong acidity vs. total particulate acidity.

The semicontinuous monitor is an optimized version of a design by George Allen. The monitor consists of three components: a variable temperature heater, a sulfur gas denuder (lead oxide-coated), and a flame photometric detector (FPD). The system utilizes a ramp circuit that changes linearly between three temperatures: less than 50 °C, 125 °C, and 300 °C. At below 50 °C, one gets a response from the FPD that is a measure of total particulate sulfur. At 125 °C, sulfuric acid can volatilize, the signal decreases, and a measure is received of total particulate sulfur minus sulfuric acid sulfur and perhaps minus other substances. Finally, at 300 °C, both ammonium acid sulfate and ammonium sulfate volatilize and the signal drops still further. Ammonia is added at two locations; one is between the denuder and FPD, in George Allen's design, and is intended to provide equivalent detector response for both sulfuric acid and ammonium sulfate. The second location to add ammonia is before the heater. This ammonia addition at just a portion of the time within the 125 °C region provides both a qualitative means to improve the selectivity of the method to identify sulfuric acid (as distinct from other volatile sulfur species) and to discriminate sulfuric acid against such alternatives.

The AIHL studies included evaluations of both single components and external aerosol mixtures. A major concern was, relatively volatile sulfur-containing species acting as potential positive interferants in the method. Hydroxymethane sulfuric acid, the adduct between formaldehyde and sulfur dioxide, was found to be indistinguishable from sulfuric acid in the system, and its ammonium salt was ammonia, indistinguishable from ammonium sulfate. However, the continuous monitor can be used to measure sulfate.

Two component mixtures were also examined in which there were external aerosols. One of the aerosols was submicron sulfuric acid, and the second was a mixture of ammonium nitrate, ammonium sulfate, ammonium chloride, or ammonium bisulfate. These components were allowed to interact in turbulent mixing before entry into the monitor. The analyzer response to sulfuric acid under conditions of a constant degree of dilution is severely depressed by ammonium nitrate and also by ammonium sulfate. Because ammonium nitrate and ammonium sulfate are common in atmospheric aerosols (especially in Southern California), it is not surprising that sulfuric acid was not seen in ambient air at a limit of detection of about 1-2 $\mu g/m^3$.

Appel then discussed the effectiveness of an ammonia denuder in collecting acid particles. As part of the SCAQS study, sampling was conducted during the summer of 1987, using two low-volume samplers that were nearly identical. One had an ammonia diffusion denuder of parallel tube design with phosphorus acid coating. Subsequent sample handling was done in a glove box arrangement in the field with the addition of the distilled water extractant. Strong acid was measured as the antilog of the pH. Total particulate acidity was measured by titration to pH 6.5.

If the results for the two samplers are compared, substantial scatter is seen with a modest correlation of about 0.7. For the ratio of means, there is a slight 10% bias in favor of the unit with the denuder, but the difference is not statistically significant. Thus, under the relatively low acidity conditions that exist in California's South Coast Air Basin (SCAB), the ammonia denuder was relatively ineffectual.

If measured strong acid is compared expressing the results in micrograms per cubic meter as sulfuric acid against total sulfate, it is discovered that at most 20% of the strong acid might be accountable by sulfate-containing acids. The rest appears to be contributed by organic acids.

Appel drew both positive and negative conclusions from these studies. Interfering substances inhibit the continuous sulfur monitor for sulfuric acid. Ammonia addition to the inlet of the sulfur monitor can be a useful strategy. Free sulfuric acid concentration is very low in the California's SCAB and nonsulfur acids appear to be major contributors to acidity in the SCAB. Finally, the ammonia denuder is not a useful device at the low acidity conditions under which it was used.

Appel discussed an intercomparison of the annular denuder (measuring nitrous acid) against the differential optical absorption spectrometry (DOAS) technique carried out in Southern California. In one comparison, the concentrations of nitrous acid ranged up to 16 ppb with a correlation coefficient of 0.93 between the data sets that contained 4- to 6-hour averaged values. At very low concentrations, the annular denuder method appears to have a high bias relative to the DOAS technique. Daytime concentration levels often run 3 to 4 ppb, whereas both theory and the DOAS technique say much lower levels should be measured. At relatively higher concentration levels, the DOAS method gives levels that are about 20-25% higher. The annular denuder method results were corrected by using two annular denuders in sequence, but no other corrections were made such as those for the absolute efficiency of nitrous acid collection on the denuder (which may perhaps be a 5% correction).

Discussion

Robert Stevens asked if Bruce Appel had made any correction for the possible oxidation of nitrous acid to nitric acid. Appel said no. Stevens replied that that could account for the discrepancy at low concentrations. Dr. Ivo Allegrini asked about the height at which the annular denuder method and DOAS sampled. Appel stated that they were both at the same height above similar surfaces.

BROOKHAVEN NATIONAL LABORATORY

Dr. Roger Tanner commented on some basic issues about what the population is really exposed to, how the measurement is made, and whether the measurement is sufficient. Historically, measurements have been made of free acidity or pH, titrations of various forms of acidity, and, in the absence of either of those, some estimations based on ion balance. He emphasized that size-segregated measurements are absolutely necessary. There is abundant evidence that the soluble portion of coarse particles are basic and that at least particles below 1 μm are slightly acidic most of the time. He also pointed out that acidic and basic gases do not need to be removed in the sampling inlet because if the samples are at equilibrium in the atmosphere they remain at equilibrium if the sampling is done correctly. He felt that there is evidence that in cases where there is a well-mixed atmosphere and equilibrium between aerosols and gases, the measurements can be made without removing acidic and basic gases if care is taken. Most measurements have used acid-treated quartz filters using as short a sampling period as possible. The quartz filter can retain substantial amounts of aerosol material without substantial buildup and avoid the types of interactions that often happen under other sampling conditions.

Tanner then discussed measurement techniques focusing on BNL's strong acid titrations, (Gran titrations) and discussing briefly extraction, flame photometric, and thermal evolution techniques. He noted that, as Bruce Appel had shown in his presentation, flame photometric techniques may have practical limitations.

The Gran titration is a useful way of getting a generic measurement of strong acid under atmospheric conditions and is basically the method that BNL has chosen to use. A titration is done in a solution using a constant current source under conditions in which there is 100% current efficiency. The pH is measured essentially as a function of time, the Gran function calculated, and the data reduced using a best fit of the linear portion (if there is one) of the resulting curve. The quartz filters are extracted with a microequivalent of sulfuric acid that is then subtracted using a blank procedure.

Tanner next discussed how the Gran titration plot could be used in cases when there may be contamination by weak acids. If amounts of weak acids are significant, there may be a deviation from a linear curve. Thus, if the weak acids in aerosols or precipitation are comparable in quantity to strong acids, there are problems using a straight titration. Many samples taken by BNL did not have titratable acidity; in fact, there was net soluble base in the aerosol.

Tanner showed some historical data taken using high-volume quartz filters and Gran titration during the summer of 1977 as part of a New York summer aerosol study. Significant quantities of acid were present in the summertime and the day-to-day variability was large; there was much greater variability than for ammonium. In general, acid concentration was higher in the afternoon due to daytime production.

Tanner mentioned work using a real-time flame photometric monitor of original design to measure sulfate in one channel and sulfur dioxide in the other. BNL is modifying one version of the instrument to put a heated denuder in the alternate channel and thus remove sulfuric acid so that, by the difference, one can obtain an estimate of sulfuric acid in real time. It remains to be seen whether or not the instrument is stable and sensitive enough for ambient levels in the Northeast.

Discussion

Walter John commented on the organic acids, noting that organic acids are destroyed by bacteria. Unless the sample is chilled, there may not be organic acid by the time the sample is analyzed. Tanner agreed. John speculated that when people say that they did not get interference from organic acids, their sample may have been warm and the bacteria took care of it.

George Thurston noted that Tanner had said that an ammonia denuder was not needed upstream of the sample. He wanted to know if that assumed that someone would process the sample immediately and that relatively short samples are taken. Tanner replied that there could be problems if one took long-term averages without a denuder. Robert Stevens asked if Tanner's statement was based on experiment. Tanner replied yes; they ran samplers with and without denuders in the laboratory for relatively short samples and did not find significant effects using acidic aerosols and ammonia.

ARGONNE NATIONAL LABORATORY

Mr. Stan Johnson discussed a new instrument called the real time infrared aerosol analyzer (IAA). The IAA can measure sulfuric acid, bisulfate, sulfate, nitrate, ammonium ion, water content, crustal materials (silicate, carbonate, and phosphate), and all other infrared (IR)-absorbing species in the aerosol. Aerosol samples are divided into the three size fractions corresponding to the three ambient aerosol modes. Measurements are made essentially in real time with practical time resolution of a few minutes for accumulation mode aerosol. A wide variety of sampling frequency and duration can be used.

Instrument operation is fairly simple. The sample aerosol is split in a virtual impactor. The coarse particles are brought down to a chamber where they are collected on a Teflon filter. Dr. William McClenny's method of using IR-spot spectroscopy through a filter is used to look at the collected aerosol. The accumulation mode or fine-fraction aerosol is split and brought through two separate nozzles and impacted onto an internal reflection element.

The internal reflection element is the heart of the instrument and is based on the technique of attenuated total internal reflection. In this technique, the light beam is internally reflected in an IR-transparent material and is attenuated at each reflection by material on the external surfaces of that IR-transparent material. A set of these internal reflection elements contains up to 14 separate elements. One form of time resolution can be obtained by simply stepping from one element to the next. The other type of time resolution (which is used for short-term resolution) is achieved by scanning the spectrophotometer, storing individual interferograms, and coadding them after the fact. A scan takes 8 seconds, but in practice about 1 minute is needed to collect enough material. The cut points are 2.5 μm for the initial impactor and 0.3 μm for the ATR impactor. Those particles that pass the attenuated total reflectance (ATR) impactor are then collected in another chamber with a Teflon filter. This portion is not in place at present, but can easily be added.

The Fourier transform infrared (FTIR) spectrophotometer is a very compact commercial unit with a personal computer, monitor, and plotter. There are flip mirrors on either side of the instrument so that any one of the three chambers can be observed in real time, although normally only the accumulation mode aerosol is observed in real time. The other modes would be sampled at the end of each hour.

The instrument has been used in a motor home and operated off the home's generator. The instrument seems to be insensitive to vibration or other similar problems. Johnson showed a series of spectra taken in the laboratory illustrating in situ neutralization of sulfuric acid. A dilute solution of sulfuric acid was aerosolized onto one of the elements and inserted into the instrument. In successive spectra (of 10 scans each), the sulfuric acid bands diminished as equilibrium with room conditions was approached; the water band also shifted. Thus, as the acid loses water, the amount of hydration could be obtained. After equilibrium was reached, a small beaker of ammonium hydroxide was placed in the chamber. Successive spectra showed an ammonium band arising immediately and increasing as the sulfuric acid bands shift until the spectra of neutral ammonium sulfate is obtained.

The first spectra of ambient aerosol was taken in the mobile home on January 6, 1989. It showed ammonium sulfate and ammonium nitrate. The collection time was 5 minutes with a flow rate of 70 lpm. The loading was 0.6 μg sulfate on the plate or 1.8 $\mu g/m^3$. The nitrate content was about 0.5 μg on the plate or 1.4 $\mu g/m^3$ of nitrate. The lower limit of detection was calculated to be about 30 ng of sulfate.

Johnson also showed an IR spectrum from the coarse-particle fraction collected on a Teflon fiber. It revealed a difference in the constituents for the coarse fraction, which consisted basically of phosphate, silicate, and some ammonium nitrate.

To demonstrate the capabilities of the instrument to detect sulfuric acid, Johnson showed a spectrum obtained by spraying a very dilute solution of acid into the inlet. The spectrum obtained did show the characteristic peaks for sulfuric acid. There was about 0.7 μg sulfuric acid with a lower detection limit (LDL) of about 80 ng sulfuric acid. Johnson had then taken a bottle of ammonium hydroxide and opened it by the inlet for about 10 seconds. The spectrum obtained after doing this showed completely neutralized ammonium sulfate on the plate.

Some of the advantages Johnson cited for the instrument were:

- Unambiguous identification of acid aerosol in real time
- High sensitivity for accumulation mode aerosol (50 ng for sulfate LDL)
- Capability to add or subtract different time periods (down to several minutes time resolution)

- Very low cost per analysis
- Good match of collection and analysis techniques to the size modes
- Acidic aerosol separated from basic aerosol material during collection
- System is usable from a mobile platform
- System can be automatic or interactive
- Analysis is nondestructive so sample can be used for other analyses

Johnson felt the instrument had broad application as a reference method, for monitoring (with high time resolution), in laboratory studies, for health effects studies, and in industry.

U. S. EPA AREAL

Before giving an overview of aerosol acidity measurements, Mr. Robert Stevens of EPA's AREAL first summarized some comments heard earlier in the workshop. He noted that aerosol sulfate and pH measurements have been made for a long time, and workshop participants Roger Tanner and Leonard Newman had made a career of it using quartz filters. The work that was originally done in London was based on the use of high-volume samplers and pH and sulfate measurements, and identified the health problems associated with high concentrations of these materials. There also have been studies using PM-10, sulfate, and pH measurements. These have been the most rudimentary, simple, and direct ways of obtaining the measurements without the use of denuders.

The questions workshop participants were asked to address were what is the most reliable indicator and what is the most cost-effective way of gathering data. Stevens pointed out that one of the methods for checking the consistency of data is to do a mass balance between the ions that are being measured. When measuring sulfate ion, hydrogen ion, ammonium ion, and nitrate ion and they add up to a total that balances against the hydrogen ion, a good indication is obtained for which form the sulfate took during the individual measurements. There are times when there is excess hydrogen ion, suggesting that free sulfuric acid exists. Most of the time, when looking at ambient sulfate or sulfur with a FPD, it is almost indistinguishable from total sulfur, but there are times when there is free sulfuric acid. He noted that, as Roger Tanner and Leonard Newman had pointed out, by sampling during short enough periods and protecting the sample with a denuder (regardless of whether one needs it or not), samples with free acid can be obtained. Most of the sample exists as ammonium acid sulfate. For data from the 1970s, the nitrate concentrations are exceedingly low. This could be, and probably is, due to the ignorance of ammonium nitrate evaporation at that time. As a consequence, Petros Koutrakis very adequately articulated the problems when ammonium nitrate coexists with ammonium acid sulfate on the filter. As it evaporates, that ammonia can neutralize the existing sulfate. Thus, hydrogen ion values are very likely underestimated and that may be the case for all the measurements made up to this point.

Stevens returned to the question about using Gran titration or pH measurements. He agreed with Leonard Newman that Gran titration is the best way to measure total acidity, but that one must consider the airshed that is being sampled and the complexity of the Gran titration itself. The data that John Spengler showed concerning aerosol acidity measured in the Harvard six cities study were derived from measurements performed in EPA's laboratory using Gran titration. At the same time, pH measurements were also made. There is a very positive correlation (with a slope close to unity) between the hydrogen ion concentration calculated from the pH measurements and the Gran titration extrapolated to the appropriate end point. However, all those samples were taken east of the Mississippi, a point that must be raised in assessing how to set up a national network and gather such information. It does not preclude the possible importance of organic acids. For most of the samples in the laboratory for which pH measurements are performed, the filter is immediately put into an aqueous solution or stored cold (performing the pH measurement as soon after collection as possible to minimize the problem with bacteria).

Stevens described how he learned about annular denuders and was eventually convinced of their usefulness in characterizing the atmosphere. He noted the need to understand the interaction of acid gases with aerosols on filters in EPA's program, especially for the Integrated Air Cancer Program. The application of the annular denuder to the measurement of total aerosol acidity as opposed to particle acidity provides one avenue to consider. However, the simple filter pack arrangement may still be useful. Enough data must be examined to determine if a pH measurement with just a filter pack preceded by an inlet offers any major problems for determining the hydrogen ion concentration, as opposed to a filter pack that was preceded by a denuder. Several workshop presentations suggested that there is a problem, others suggested that there is not. Perhaps some modest laboratory experiments and preliminary comparisons between the filter pack and other assemblies with existing technology are in order to determine which approach would be most beneficial to the Agency's needs.

Stevens next discussed the protocol used in his laboratory to determine aerosol acidity with a fine particle sampler. A Teflon-coated elutriator/impactor with a 50% cut point (D_{50}) of 2.5 μm is used to compare the annular denuder with a filter pack using the same cut point. Next, a 47-mm Teflon filter is used because (1) Teflon filters are very easy to extract, (2) they can be used for mass measurements and are much easier to handle than quartz filters, and (3) one can perform additional measurements such as X-ray fluorescence analysis. Next, the filters are extracted with 5 ml of 5×10^{-4} N perchloric acid solution using an ultrasonic bath and pH measured with a calibrated pH meter. Then either IC or colorometric analysis is used to analyze the filters for sulfates, nitrates, nitrites, and ammonium ions. The nylon filter is usually extracted with 10 ml of sodium carbonate IC solution and an IC analysis performed to look for nitrate.

The protocol for determining aerosol acidity with an annular denuder/filter pack is somewhat similar. There is the same inlet assembly of a Teflon coated elutriator/ impactor with a D_{50} = 2.5 μm, then a denuder coated with sodium carbonate and glycerine, followed by a denuder coated with citric acid. This is the simplest set of components one can use to compare aerosol acidity with a fine particle sampler. To measure nitric acid, a sodium chloride denuder would precede the sodium carbonate denuder to decouple the collection of nitrous acid from nitric acid. The citric acid denuder collects the ammonia. The separations are identical to the measurements that were made for the fine particle sampler with the exception that the denuders are extracted to determine the concentrations of sulfur dioxide, nitrous acid, and nitric acid on the first denuder and ammonia on the second denuder.

The housing that is now available for use in many field studies will allow for two denuders in one assembly. For the tests that are being performed at EPA, a fine-particle sampler is used along with the annular denuder. The denuders are run for about 23 hours and then extracted and analyzed. The system with the citric acid denuder consistently reads a lower pH value than the system without the denuder indicating that there is some ammonia in the atmosphere.

Stevens concluded by noting important issues that need to be addressed. Stan Johnson's discussion on the FTIR internal reflectance analyzer for sulfuric acid and ammonium bisulfate looks very interesting and is one the Agency should consider using to compare against other results. The workshop participants will have to examine various approaches and try to decide what assemblies should be used and in what directions to proceed. It will be difficult for the four committees to make this decision and narrow down the choices so that a manageable research program can proceed.

Discussion

Peter Mueller asked if anybody had a standard procedure for analyzing sulfuric acid on Teflon filters following an ammonia denuder. If so, he wanted to have it. Stevens replied that at least three persons were using the same procedure and he would give a copy of the procedure to Mueller.

SECTION 8

SELECTING ACID AEROSOL INDICATORS

OVERVIEW

William Wilson pointed out that comments made earlier might be confusing to people who did not have a good understanding of atmospheric chemistry and atmospheric dynamics. He then discussed some data from BNL showing acid patterns on a 6-hour basis. There was acid in the noon-to-6 p.m. period, but not in the midnight-to-6 a.m. period or the 6 a.m.-to-noon period and, in some cases, not in the 6 p.m.-to-midnight period. Discussed earlier was whether or not a denuder is needed to remove ammonia; in certain places and times, a denuder was not needed. Certainly, in a part of the country where acid always exists excess ammonia will not appear, and a denuder is not needed. Also, with brief sampling times, sampling an aerosol at equilibrium is likely and again, a denuder is not needed.

Problems arise with longer sampling periods (such as a 12-hour or 24-hour sample) or periods of different equilibrium aerosols. Ammonia is generated at the ground level and has to rise to mix whereas sulfate is formed throughout the atmosphere (in some cases above the ground-level mixing layer during the night) and has to sink to mix. Thus, two factors cause sulfuric acid to be high in the afternoon. One is that it is generated during the day and the other is that there is sometimes a reservoir that allows the sulfuric acid to mix downward. If samples are taken as a 1-hour slice in the middle of the afternoon, an ammonia denuder is not necessary. However, with a 24-hour sample, in the afternoon sulfuric acid might be collected, but in the evening ammonia will be collected since there is excess ammonia at night. Then, without a denuder, the acid will be neutralized on the filter.

Wilson then asked the panel to discuss the correct indicators for acid aerosol, to put the issues into perspective, and to clarify some of those issues to be discussed the next day in the group sessions. Each panel member was asked to comment in turn.

PANEL DISCUSSION OF KEY FACTORS

Morton Lippmann

Lippmann stated that some of his thoughts have already been expressed. Two kinds of health effects could occur at current ambient levels. One is an acute response in terms of bronchoconstriction. The focus would then be on asthmatics as the sensitive population and the concern would be about peak exposures. Even then, he felt the indicator did not have to be based on sampling for times as short as minutes or even an hour; what little evidence there is suggests that the response is still accumulated over periods of a few hours. However, Lippmann felt that if acid were controlled to the point of protecting against the chronic effects (which he viewed as the more significant public health issue), it would inevitably control against the less serious case of the acute and reversible bronchoconstrictive effects. Thus, his recommendation would be to focus more on the longer-term indices that take into account C x T products. For a start, even a seasonal average NAAQS would be adequate. It would deal with the kinds of symptomatic effects seen in the Harvard six cities study and that may be occurring elsewhere. Preliminary indications from the 24 cities study appear to be consistent with those seen in six cities.

Lippmann felt that an annual average is probably not as sensible as a seasonal average because people are outdoors more in the summer when the acid levels are generally higher. He would not focus the strategy on center-city sampling alone because (like ozone, the other major secondary air pollutant) there are greater exposures outside urban centers because ammonia sources in major cities reduce acid exposure. Thus, acid tends to be higher away from the center city and therefore it affects more people. Although people are concentrated in center cities, there are more people, in total, away from center cities. To get the process started and to focus on what may be the most serious issues with respect to health effects, i.e., the chronic issues, Lippmann suggested monitoring to determine the seasonal average concentrations or perhaps annual average concentrations. This would mean longer-term sampling, although it would not have to be every day. Good estimates of seasonal or annual averages could be obtained by sampling every second or third day. Lippmann emphasized that the health effects data driving this need for a monitoring method indicate a deep lung response that only the acid particulate can produce (soluble acid vapors cannot and the weak acids would not). Thus, strong acid in aerosol is the index to investigate.

John Spengler

Spengler commented that the measurements are actually serving multiple purposes. From an epidemiology point of view, this measurement is serving as a surrogate for dose. All the reactivities that may occur on filters are significantly more complex on inhalation. Thus, no matter how well defined, the actual atmospheric measurements may be still a surrogate. Spengler hoped that the design of these studies would pursue the dominant acid species produced by automobiles and fossil fuel burning. Because epidemiology is a blunt instrument, he felt the need to ensure that a consistent system is used and the dominant species are captured so that false attribution of effects, should they occur, is not made. This must be done with a great deal of care to ensure that at least the two major components have been characterized.

Spengler felt that clinical studies might dictate very different needs and may be more attuned to atmospheric scientists' interest in understanding the detailed chemistry at sites as well as within the sampling systems. He also felt the clinical data were confusing. This data might be due to particles or to some reactions within chambers, face masks, and upon inhalation. Attention should be paid to such details to best define the real dose to the population. In epidemiological studies, this is only done by approximation. Spengler also noted the need to avoid major confounding biases such as the contribution from indoor air or the modification of exposures by virtue of human activities.

Dr. George Wolff

Wolff emphasized two points that had been brought up earlier and raised other ideas that he had considered as a member of CASAC. The first point is one that Morton Lippmann had pointed out earlier. CASAC reviewed the health effects data and recommended focusing on submicron acid particles forming an aerosol that is composed primarily of sulfate. Neither acid gases nor coarse acidity (the acidity found in fogs) are candidates for a standard. The committee realized that ideally the most useful method would be one that could speciate the acids, but also realized that it probably was not possible at this point. A measurement of total strong aerosol particle acidity seemed a reasonable compromise.

CASAC provided a research plan containing recommendations that EPA seems to be following since one of the first recommendations was to hold this workshop. CASAC first wanted to identify the methodology that could be used to establish a monitoring program to determine: (1) whether or not the levels of acid aerosols found across the country warrant a standard, and (2) the spatial and temporal distributions of the acid aerosols. Thus, if a standard was determined to be necessary, a nationwide routine monitoring network could be designed for which a relatively simple and inexpensive to operate sampling technique would be needed.

Wolff stated that the other monitoring network that was mentioned was envisioned as perhaps a 1-year network at five different locations chosen to investigate cities that are affected by different types of climatology. Selection certainly is negotiable; one should be in the northeast, one in the midwest, probably Houston, definitely Los Angeles, and maybe another one. In the first year, monitoring networks would be established (each with 5 to 10 monitors) within these geographical areas to characterize the spatial distribution within, downwind, and around these urban areas. At the moment, there is no data to indicate where the critical sampling locations might be within a given urban area.

Wolff remarked that to understand the mechanisms that control the spatial and temporal distributions, a host of other species must be measured: nitrogen, ammonia, and sulfate, as well as the acid and some others. For the other longer-term routine monitoring network, only the acids might be measured. Wolff emphasized that the workshop participants need to provide guidance in two different areas. One is for the longer-term nationwide routine network using a simple, inexpensive method (without measuring a host of other variables). The other is for the special network that would run for about a year. The issue is what variables to measure and how to measure them to optimize the information gathered from that network.

Dr. Sam Morris

Morris emphasized the need to investigate the actual population exposure as opposed to ambient concentrations. This implies characterizing urban areas to demonstrate that their exposure is lower than more suburban or rural areas. It also means evaluating indoor concentrations because potential indoor sources could cause higher levels and because indoor levels may be lower than outdoor levels. Since people spend most of their time indoors, that sort of population exposure information will be important and should be included in an exposure assessment as EPA has done for ozone and carbon monoxide. In those cases, EPA is taking into account population activities and time sequences of exposures.

Morris also felt that the more detailed monitoring should come before choosing the simple method to determine what species are actually important, whether the C x T relationship holds at lower levels, and whether or not total acidity is a reasonable indicator. Thus, it is useful to have as much information as possible about both human exposure and health effects. Morris also felt that monitoring other components is very important. Either compounds that may interact with acid aerosols like ozone, or compounds that can interact in different ways like sulfur dioxide, or some of the acid gases that presumably will act to neutralize the ammonia in breath might affect the impact of the particle acids. Similarly, most of the health effects studies are based on short-term exposures with short-term effects. It is too early to look at a seasonal or annual average, which should be considered later as more detailed information becomes available.

Al Wiebe

Wiebe noted that the AES is really interested in the methodology to measure particle acidity because it is important in the acid rain issue as well. He felt that there is a significant amount of data now available from cities and other studies at least for sulfate. He thought enough information might exist to estimate the fraction of acid particles because several small studies have looked at particle acidity. If the results of acidity studies could be extrapolated to larger sulfate data bases, short-term studies were possible to show how to relate an unknown parameter to a measured parameter. He cited an example in which originally unmeasured pH could be inferred from other indicators for early acid rain studies. Finally, Wiebe mentioned the great need for a standard methodology to measure acid particles in order to compare the results of measurements.

Mr. John Haines

John Haines of OAQPS disagreed with Morton Lippmann about the need to characterize peak acid aerosol concentrations. Haines thought that understanding the peaks is necessary to help design controlled human studies, and 12- or 24-hour values should not be the entire focus of measurements. It may not be necessary to monitor peaks on a continuing or regular basis, but some short-term studies to determine how the peaks relate to a longer averaging period would be helpful. Haines also noted the need to understand the role of ammonia, obtain good emission inventories for it, determine its ambient concentrations, and determine how these aspects interact and affect one another because ammonia is an important factor affecting population exposures within urban areas.

Haines said that some characterization studies in larger cities would be necessary even though current opinion is that acid aerosol is not a problem there. The public at large will want to know that there are data to support the hypothesis that it is a nonurban problem. There is also the general need to characterize acid levels in the ambient air so that the information can be used in health studies.

Dr. Lester Grant

Grant of ECAO drew upon ECAO's past experience preparing EPA criteria documents. He noted that typically, when starting to develop or approve methods for ambient monitoring, a series of experiences occur that include some real surprises upon going from the laboratory into the field. Grant emphasized the need for careful validation of the procedures in both the laboratory and the field. He noted that the Harvard group and others have extensive experience with particular approaches. As other approaches are developed, it is absolutely crucial to pay attention to what is happening and why. It cannot simply be assumed that what works well in the laboratory will work in the field; experience says it almost certainly will not. The value of the data obtained by expending tens of millions of dollars may depend on how carefully the methodology, intercomparisons, and follow-up evaluation of monitoring results are designed and implemented.

Grant also discussed additional reasons to carefully consider interactions with other pollutants. He pointed out that interactions or potential interactions must be examined not only in a general sense, but in terms of how the sequence of exposure to these different pollutants can affect health effects. For example, the observed health effects might be highly dependent on whether ozone exposure occurred first and then an acid aerosol exposure, or vice versa. This obviously complicates monitoring studies that use 12 to 24 hours as the averaging period for the acid aerosol measurement. Other averaging times may be more appropriate for other pollutants. Studies must be designed so that the data can be examined and the sequence of exposures determined.

Grant suggested possible studies in other cities around the world that have higher pollutant levels than those in the United States. These cities may represent targets of opportunity to build upon research (underway or contemplated) for monitoring or health effects studies. Adding a component to monitor acid aerosols may provide some very important information, e.g., about very high peak pollutant levels in cities such as Sao Paolo, Brazil, that rival those in London in the 1950s. Grant also noted that whatever is done in the United States to develop these methods, use them in the field for routine monitoring, and relate them to epidemiology studies and health end points, will ultimately be used internationally to establish standards in other countries.

William Wilson

Wilson observed that he had heard of at least five different types of monitoring programs needed within the acid aerosol program. All of these may require different quantities of indicators, types of indicators, or timing. There may also need to be different kinds of monitoring. He urged participants to discuss in group sessions the different types of monitoring, from long-term measurements to support epidemiology studies to very detailed measurements, to help develop models.

Additional Panel Comments

William Wilson asked the panel if there were any comments on the problem of breath or endogenous ammonia and whether it could lead to the neutralization of sufficient sulfuric acid to produce a threshold effect level. Morton Lippmann noted that he had commented on that earlier. The neutralization seems to be time-limited; the fractional neutralization by ammonia is not dependent on concentration and would not, therefore, create a concentration threshold. The results indicate that some fraction is neutralized, but it is not concentration dependent. Although it is an issue that needs more evaluation, it does not prevent effects occurring at very low concentrations.

Lippmann clarified his earlier comments that he was not trying to exclude needed research. Because resources are limited, he wanted to state which items were most important, not necessarily the only important ones. He agreed with Sam Morris; to understand the inhalation of acid aerosols, indoor exposure should be examined because the chronic (or the cumulative) exposure is most important. Even if indoor concentrations are a fraction of those outdoors, if someone spends 90% of the time indoors, they may have more acid exposure indoors than outdoors.

Lippmann reiterated that the studies of primary concern to CASAC were studies of chronic effects. Although there is much literature about acute bronchoconstriction for many pollutants, there is uncertainty about how to interpret it. The 1-year rabbit study of chronic effects was one of the major studies of concern. The six cities study was a long-term study. He emphasized that he did not intend to exclude inner cities, but simply to ask that the large populations outside of cities be considered.

Lippmann responded to Al Wiebe's comments about data reconstruction. He noted that George Thurston and a graduate student were trying to make quantitative estimates of past acid exposure for London. The work shows a high correlation between a combined index of measured quantities and measured acid in the 1964-1972 period. Hopefully, the extrapolation can be extended using a combination of British Smoke, sulfur dioxide, temperature, and humidity. He noted that comparison measurements closely correlate with predictions and that the method could be used to estimate past acid levels. The technique will be extended to the Southern Ontario data base where acid levels and other relevant environmental data have been obtained to determine any cross-correlation using multiple regression relationships to construct past levels of acid.

John Spengler was concerned about focusing entirely on the acid aerosol that consists mostly of sulfuric acid and other sulfur species. He mentioned several reasons why this focus might be misplaced: large reductions in future sulfur dioxide emissions may affect the competitive atmospheric chemistry, nitric acid may then dominate in large urban U.S. areas, and nitrous acid may dominate indoor exposure. It could be shortsighted to ignore the potential for exposure to nitrogen oxide-based acids simply because current thinking says that these gaseous acids are removed in the upper airway and should not produce effects; current thinking is based on very little data. In addition, if the body has to overcome the buffering capacity of the mucociliated region, then it may be important to still consider gaseous acid.

George Wolff answered Spengler that this had been discussed extensively at CASAC meetings and excluded from further consideration. However, if the network (looking at five cities for 1 year) is conducted correctly and the recommendation is made to measure these other acid species, data will be obtained to judge whether or not nitric acid is important. Then, if Spengler's concern comes to be, nitrogen species can be reconsidered. Spengler responded that nitric acid exposure may be large; in many cases it is higher than sulfuric acid exposure and it dominates exposure in the Los Angeles area.

Morton Lippmann tried to clarify the issue of exposure to other acid species. He noted that concern about acid aerosols is derived from a constellation of effects demonstrated in animals and humans. These effects are related to a particle hydrogen ion; it does not mean that there should not be a NAAQS for acid vapor. However, that should be based on demonstrated adverse health effects by acid vapors. The research proposed for acid aerosols may help define the effects of acid vapors and perhaps lead to another NAAQS for acid vapor. However, the NAAQS for acid aerosol is driven by demonstrated effects and concern about highly plausible effects that warrant a public health response.

Paul Lioy suggested that if exposures such as those Spengler has speculated about are found, that might be the time to reconsider the nature of the exposure. He felt that the study design that CASAC recommended for measuring a suite of compounds could be very reasonable. That is not ignoring the issue; it is a very reasonable approach. Lioy stated that the predominant issue is that CASAC wants to address the question of whether or not there is an acid aerosol problem in the United States. This includes the need for an ambient air quality standard for acidic particles. If diverted by other issues, there is the risk that in 1-2 years, after a considerable expenditure of money, CASAC's question may not be answered and that would be a serious error.

Peter Mueller told Lioy that his question can be answered by looking at the CASAC document (CASAC, 1988). It states on page 2 that more studies are needed to establish the nature of the various health effects of acids, and it lists acids and co-occurring pollutant interactions as a medium priority research need under Section 4.3.2 (page 11).

Leonard Newman raised a fundamental question about the utility of any monitoring for acid aerosol. He could understand monitoring for a seasonal number for lead or even for sulfate. Monitoring of acid aerosol could be difficult since the material in the air is sometimes basic and sometimes acidic. The net measurement could then result in neutral or even basic aerosols. Because the body reacts when it has been exposed to acid and does not when exposed later to base, usable information cannot be obtained by averaging. If all times when there is alkaline aerosol are excluded, how are the time scales for monitoring to be chosen? Is monitoring to be done on an hour-by-hour basis for 24 hours with periods of negative or alkaline substances subtracted? Even a 24-hour sample cannot be taken and useful information obtained. One possible answer might be to accept sampling the acid aerosol below a certain size fraction. It might not give the total acidity, but below a certain particle size cut the aerosol is almost never alkaline; that size cut might be below 1 µm or 0.5 µm. George Wolff responded that some size separation is a foregone conclusion. Newman agreed, but it will have to be a smaller cut than what is considered normal because alkalinity below 2 µm is possible.

George Thurston noted that any routine monitoring network for acid aerosols must be national in scope. If a filter technique is used to take acid aerosol measurements, there would be concern about the loss of acidity with nitrates and artifacts. In that case, denuders are preferred to collect the ambient nitric acid, and a series of denuders would be needed to properly collect the acid aerosol in a location with nitrate problems. This is consistent with the issue John Spengler raised. Thurston gave as an example the system he uses that has a nitric acid denuder. Although the denuder is not extracted and analyzed for his study, it could be. Thus, if hydrogen ion is to be measured according to this filter method and it is to be done properly for national application, the instrument will likely have a denuder to collect nitric acid. Then it would just be a question of funding to extract and analyze the denuder.

Spengler responded that his thinking has a broader scope with political implications. Finally some segment of society has crossed a big hurdle and is paying attention to the fact that people breathe acid aerosols and acid gases. If the momentum goes to sulfur dioxide, a sulfur dioxide reduction bill may go through Congress. Now, the chemistry of the atmosphere, the competitive chemistry between the nitrogen oxides and sulfur dioxide, is changed. Will there then be a nitrogen oxides problem? In the future, will efforts to control acid vapors be ignored because of lost credibility? William Wilson stated that Spengler's point was well taken. A similar issue has been fought for the last 10 years by the acid deposition people. Should one concentrate on sulfur dioxide, try to get that removed, and not cloud the issue by talking about other things; or should a broader view be taken because nitrate is known to contribute acid too, and should both be controlled at the same time? Wilson replied to Spengler's question that the issue has not been resolved in 10 years and that the debate is continuing.

Dr. Tom Dzubay asked Sam Morris if he had heard that short-term effects were investigated in clinical studies and that it was too early to be concerned with seasonal effects. Does that contradict Morton Lippmann, who said that chronic effects and seasonal effects are the main issue? Morris replied no, he would not argue that the chronic effects are the more important effects. In the Harvard six cities study, the annual average for acid aerosol was correlated with chronic effects. However, the population received a whole-spectrum exposure of peaks and valleys. Possibly what was seen is a series of peak effects that persist; the more peaks, the more persistence. It is premature to disregard the peaks and valleys and only consider the annual average. John Spengler agreed with Morris about the issue of the seasonality of exposure. It is likely that over 70% of total acid exposure in the Harvard study occurs in a couple of months. He felt that this could lead to seasonal or dynamic emission controls as a viable future control strategy.

Petros Koutrakis stated that acid aerosol acidity cannot be extrapolated from the sulfate data. As indicated in the Harvard six cities data shown earlier, estimates would be off by 30 or 40%. Thus, it may not be appropriate to derive acidity from sulfate data. He also commented about the issue of a size cut. He stated that he used a 2.5-μm cut and never found alkaline particles in that range. He also expressed concern that by focusing on sulfur dioxide chemistry one excludes the western United States where there are indications of nitrogen oxide-based acidity. Studies by the Harvard group indicate that there are significant acid vapor indoors. Since a complete technology is available that permits the measurement of all these components, it should be done.

Robert Stevens noted that Ivo Allegrini had told him that concentrations of sulfur dioxide were in excess of 600-700 $\mu g/m^3$ in Milan. If he were an epidemiologist, he would like to see the hospital admissions data.

George Wolff noted that several people had commented on high concentrations of nitric acid in western cities and urban areas. Except for Los Angeles and the data generated in SCAQS, he knew of no urban areas shown to have high concentrations of nitric acid. The concentrations seen for areas outside of Los Angeles have been on the order of 1-2 ppb for the afternoon peak. He asked if other data were available. Petros Koutrakis answered that the Harvard study shows that in terms of total acidity exposure, 80% is derived from nitric acid and nitrous acid. Robert Stevens agreed with Koutrakis, but noted that the percentage included nitrous acid. In a study in Boise, ID, and ongoing studies in Raleigh, NC, there were times that 2-4 $\mu g/m^3$ for gaseous acid were measured over a 24-hour period. In more recent measurements, the nitrous acid concentration was about 2.3 $\mu g/m^3$, the nitric acid concentration 2.7 $\mu g/m^3$, and the sulfate concentration was only 3.7 $\mu g/m^3$.

William Pierson wondered if the respirability of the ammonium particles was known. The argument had been made that hydrochloric and nitric acids are not of concern because they are gases and they do not penetrate the deep lung. He felt that there is probably a part of the particle size distribution about which the same could be said. Thus, the portion of the particle size distribution that does not penetrate the deep lung must be considered. Morton Lippmann responded that the question has been investigated. The acid aerosol is generally below 0.5 μm, and it will grow hygroscopically by a factor of 2 to 3. However, for particles that grow in size to about 0.1 to 2 μm, there is no difference in deposition pattern. At larger sizes or at smaller sizes, deposition is dependent upon particle size. But in this middle range, where there is very little intrinsic motion by inertia or diffusion, it does not make any difference.

SECTION 9

SELECTING ACID AEROSOL INDICATORS - GROUP DISCUSSIONS

On the second day of the workshop, participants were divided into four working groups to make recommendations about the following issues concerning acid aerosol indicators:

- indicators for characterization and exposure studies, health studies, indoor studies, and fixed-site monitoring
- pH vs. titratable acid
- the need to measure sulfate, nitrate, and acid gases (such as nitric and nitrous acid and ammonia)
- measurement frequency, duration, and averaging time
- other areas of concern

Group assignments may be found in Appendix C. The leaders and facilitators for each group are given below:

GROUP	LEADER	FACILITATORS
I	John Watson	Tom Ellestad
II	Walter John	Jack Shreffler
III	William Pierson	Dale Pahl
IV	Howard Liljestrand	Tom Dzubay

After approximately 2 hours of discussion, group participants returned to the main meeting room to hear summaries of each group's recommendations, followed by an overview of group recommendations and further discussion.

GROUP I

Dr. John Watson reported that the group considered each topic in the order given, after classifying topics into two categories: (1) the extensive, characterization-type studies and (2) an indicator for the health studies, which focused on fine particle acidity. The group thanked George Wolff for clarifying the objective of extensive, characterization-type studies: to determine factors that govern outdoor acidity.

For the characterization studies, the group felt that the full range of measurements would be necessary to determine the factors governing outdoor acidity. With that as an objective, very few compromises can be made. However, if one includes nitrogen oxides, nitric acid, particle nitrates, ammonia, total acidity, sulfate, sulfuric acid, and organic acids, the study resembles the SCAQS. That study lasted approximately 17 days and cost $8 million excluding costs for data interpretation. Obviously, further thought is needed regarding complexity and cost, but the study will require an extensive effort.

The group also considered additional measurements necessary for studying exposure. Current activity patterns and current methods of reviewing indoor/outdoor exposure ratios should be examined first to determine whether or not the resulting information should be included in any of these additional exposure studies.

The group then focused on health-related studies emphasizing fine particle acidity. Two types of acidity were discussed: strong acidity and so-called weak acidity. The group felt that both were important and that both could probably be determined by a pH measurement. Bruce Appel and Petros Koutrakis were very helpful in these discussions. The consensus was that the strong acidity has an operational definition, as does total suspended particulate, i.e., the dissolution of the sample in 10^{-4} N perchloric acid solution and measurement with a calibrated pH electrode. Evidence presented in the group, particularly from Koutrakis's study, showed that, at least in the East, no great difference was obtained between a titration and a pH measurement. However, making both types of measurements should be left open as a possibility. Both the strong and the weak acidity could be included, not only to accommodate the East and West, but to obtain a broader idea of what these exposures might be. The group felt they needed more guidance from the health effects experts to know whether the weak acidity was important. The consensus was that both of these measurements could (and very likely should) be made if a proper procedure is developed.

Group I also discussed health studies, but only to identify potential interferences that should be measured along with the acid indicator. These included ozone, nitrogen dioxide, sulfur dioxide, and ammonia. The group designated the acidity indicator as "fine-particle, soluble hydronium," which seemed preferable to "strong acidity."

The group also discussed additional measurements, especially for acidity, needed for indoor sampling. The question of fixed-site monitoring was translated into a question of how to determine what people are actually exposed to rather than what concentrations are measured at a fixed site. Some measurements are dictated by the measurement technology. In the past, such measurements of nitrogen dioxide and sulfur dioxide could be made, but now there are new ways to make active measurements of fine particle mass, strong acidity, and ammonia. Thus, one part of the characterization study should include a personal exposure, to verify that one could derive personal exposure from concentration measurements at a fixed site, modified by a series of exposure estimates for a typical person for different activities throughout the day.

The group then discussed the issue of pH vs. titratable acid. The group's assessment was that, properly sampled, either could probably achieve equivalent results under most circumstances. The real question concerns the practicality rather than the feasibility of these two types of measurements. In general, it was felt that, depending upon the solution, the pH-type of measurement could give results for both the weak and the strong acidity and would probably be a more cost-effective approach. However, costs and accuracy should be compared before reaching a final decision. Alternatively, if these methods can be shown to be equivalent, both of them could be allowed as measurements.

Group I felt that measurement of sulfate and nitrate (as well as ammonium) is needed for any type of intensive characterization study, but probably is not needed for measurements that characterize only health effects. Health effects measurements would be desirable, however, to relate new measurements to past data bases. Subsequently, to enhance a larger-scale health-related measurement, relationships between the strong acidity and these species could be established and that information used to infer the acidity that might have existed in past studies.

Measuring acid gases was felt to be essential for any type of a characterization study to determine these gases' effects on the measurement process. The group unanimously believed that the ammonia must be removed from any sample using a denuder or similar device. However, the nitric acid might not affect the strong acidity of the samples. For health monitoring, it should not be necessary to monitor these gases on a routine basis. However, in comparison evaluation studies, the potential for these gases to interfere with the measurement needs to be examined more carefully.

Measurement frequency, duration, and averaging time were divided into two classes. One class is the intensive studies. The group talked about a diurnal profile that would be taken at a smaller number of sampling sites. Up to five different samples a day would be taken of the different species, with 24-hour samples taken every day to evaluate routine monitoring. So, imbedded within the larger-scale characterization study of 24-hour samples would be a few sites (and a few intensive sampling periods) with shorter sampling time periods. For hydronium health-related measurements of the strong, fine-particle hydronium ion, it is important to determine whether or not different constituents have different equilibria during different parts of the day (leading to neutralization during certain time periods). Thus, the minimum duration should be 12 hours, two samples per day (preferably more), until one verifies that at a particular site and season a portion of the sample taken during one part of the day does not negate a portion of the sample taken during another part of the day. The sampling frequency should be approximately every other day.

Discussion

Leonard Newman questioned how, with a single pH measurement, both strong and weak acidity could be obtained. Bruce Appel responded that it could be done by splitting the sample and treating the two parts differently.

GROUP II

Walter John was the leader for Group II. Because the group was unable to make distinctions for the first three questions concerning indicators, they developed instead a prioritized list of indicators. The group agreed that particle strong acidity is the highest priority. There was a consensus that the word "particle" be defined as "fine particle," to eliminate coarse, alkaline particles. The prioritized list of indicators follows:

1. fine-particle, strong acidity
2. sulfate
3. ammonium ion
4. nitrate
5. ozone (because other variables are needed that are important in health effects studies)
6. sulfur dioxide and ammonia gas
7. nitric acid (there was some discussion of nitrous acid)
8. organic acids

Acidic gases can easily be added because denuders are used before filter packs. Most members agreed that denuders were necessary, although about 3 out of the 15 disagreed. The denuder, of course, will also easily measure ammonia gas and acid gases. The group felt that the indicators for the fixed-site monitoring would have to be broken into a minimum set. However, it seemed premature to decide which indicators to include in that minimum set. That decision should probably be postponed until more data are available. Group members stated that considerable data exist already that should be examined and, if possible, included in the data set.

The issue of pH vs. titratable acid was probably the most difficult question of all. There did not appear to be a group consensus, although the majority said that titratable acid was preferable. The group felt that titration is not significantly more difficult to do than a simple pH measurement, yet it gives more and better information. However, the opinion was expressed that strong acid is what needs to be reported. It was noted that the sample needs to be kept cold so that the organic acids remain in the sample.

Regarding measurement frequency, most group members felt that 24 hours is reasonable for monitoring. For the more intensive studies and for the first studies, shorter time periods were preferable. The 12-hour period is a natural period because it covers the diurnal cycle of most of the pollutants of interest. The duration or the frequency should be at least every 3 days for the initial studies (those in the first 3 years). Six-day durations would miss some episodes, and it would take longer to accumulate the data set. There was a minority opinion that measuring every 3 days or less is difficult to accomplish and that 6 days might be more practicable.

Discussion

Petros Koutrakis raised the issue that the Gran titration may require more sample volume than the pH measurement. Robert Stevens felt that was a technical problem that could be dealt with in later discussions. However, Bruce Appel said that a decision was needed on whether titration could be eliminated and only a pH measurement used. Walter John noted that there were also questions about whether the solution should be preacidified (Bruce Appel agreed). Walter John stated that extracting with an acidified solution also affects the ability to measure near neutral samples. It was noted, however, that EPA had stated earlier that it could easily accommodate more than one solution. George Thurston asked if, when referring to titratable acidity, one meant a Gran titration or an end point titration. Walter John responded that most people refereed to Gran, but there was such a diversity of opinion that the issue needs more detailed study.

GROUP III

Dr. William Pierson noted that the group added a few issues to those they had been given. These included particle size, a definition of terms, sample preservation, time resolution, and detection limit. The group made no distinction between the indicators for purposes 1 to 4, choosing instead to discuss what the key indicators should be. The group considered particle size (mass median diameter [MMD] and geometric standard deviation (σ_g) at the entrance to the breathing zone) to be important because there might be a difference between 0.3- and 0.85-μm particles. Also, from the standpoint of acidity, a size cut at 1 μm will reduce alkaline particles. This also requires size information. The next thing needed was concentration of strong acid (the hydronium ion), time of exposure, and their products. Time resolution was needed for two reasons: (1) to evaluate acute physiological effects (to approach the real-world exposure assessment by a certain time in the study) and to interpret epidemiological studies (analogous to the ozone situation); and (2) to ascertain what the acid exposure is even though it is to be averaged over a season. Detection limits were discussed, and the group decided that 20 nmol/m^3 of hydrogen ion (or about 1 μg/m^3 as sulfuric acid) would be a good detection limit to use in the field. The group felt that it was important, at least in the initial studies, to do an ion balance for the hydrogen, sulfate, and ammonium ions. The ammonium ion could also be a secondary indicator for atmospheric acidity.

Group III decided it had insufficient information to determine what the particle size cutoff should be. It recommended experiments to determine the appropriate cut point to avoid alkaline material and to obtain information about σ_g.

Regarding pH vs. titratable acid, some felt that further experiments to assess the method of additions might be worthwhile. Three alternatives were considered: pH measurement, Gran titration, and total titratable acidity. Some mention was made that new instruments are being developed to measure speciated sulfuric acid and ammonium bisulfate; these instruments may nullify the question of how to measure the hydrogen ion. Using existing techniques, the pH measurement will work for the objective that has been defined, so will total titratable acidity and Gran titration.

The group also discussed the preservation of samples. Analyzing the samples on site would be a good idea, if it is possible, and would prove advantageous for measuring acidity by pH. The group felt that it was necessary to seal the samples, analyze them quickly, and perform extraction at the end, rather than the beginning, of the storage period.

Opinions varied on the issue of species to measure. The group agreed that ozone should be measured, that acid gases were a lower priority, but that nitric acid should be included. All other species should, perhaps, be included in some comprehensive stations. Here there was no consensus, nor was there a consensus on the need to measure ammonia. The need, if there is one, was to use ammonia to decide location and timing of the potential for strong particle acidity. The group thought sulfate, but not particle nitrate, should be measured.

GROUP IV

Dr. Howard Liljestrand reported that the group was unwilling to adopt the CASAC approach, feeling that it would be more expensive than CASAC thought to measure what was needed, and that studies should proceed with the more extensive approach even if it was more expensive. There was a remarkable consensus. Although there is a strong mandate to proceed, flexibility is needed and both quality assurance (QA) and health impacts must be considered. Members from both the East and West agreed that the Los Angeles model probably does apply to the eastern United States.

Liljestrand reported only the highlights of the group discussion because many of the points were covered by the other groups. The group wanted a total speciated (gaseous and particulate species) measure of atmospheric acidity. Accurate measurements of particulate acidity (for QA) are likely to require the use of denuders for both ammonia and nitric acid. If ammonium and nitrate must be measured on the aerosol filters, it would also be possible to measure them on the denuders to get the gaseous and the particulate species. It is important to measure these gaseous species to obtain better estimates of what the dose will be deep within the lungs. The acid gases will take up some of the ammonia that is released by the lungs. Thus, this may be important in determining how well the acid aerosol or acid particulate matter is buffered before it penetrates deep into the lungs and in estimating the impact on the upper respiratory tract.

For specific measurements, Group IV presumed that measurements would supplement those of existing continuous air monitoring stations, including the usual data for ozone, sulfur dioxide, and nitrogen oxides. In measuring particulate acidity, the group discussed the size cut and decided that less than 2.5 μm or down to less than 1 μm might suffice, although further study might be necessary. Species to measure included strong-acidity hydrogen ion, ammonium, sulfate, and nitrate; the gaseous species nitrous oxide, nitric acid, and ammonia; and, lower on the list of priorities, organic acids and the speciation of the sulfate within particulate matter.

For indoor measurements, the group also wanted the same measurements, with the addition (suggested by John Spengler) of supporting measurements to identify sources of systematic, nonrandom biases to predict indoor/outdoor exposure ratios.

For measurement frequencies, Group IV agreed with the other groups that a 24-hour sample was probably not sufficient. Less than 24 hours is needed to obsecure peaks in concentrations. There was some discussion of having two samples, an 18-hour and a 6-hour sample, with the 6-hour sample designed to assess the peak and the 18-hour sample to assess the rest of the day. The group felt strongly that intensive sampling should be done down to 3-hour intervals (but not routinely) to (1) ensure that the sum of the concentrations over time is equal to the average concentration obtained for a 24-hour period, and to (2) obtain frequency distributions to develop standards and determine health effects.

The group considered sampling more frequently than that; however, the 3-hour limit was regarded as a practical limit for existing technologies and detection limits. Sampling times of 1 hour or less would require developing new instrumentation.

Finally, the group considered the issue of pH vs. titratable acidity. Members agreed that the initial pH may not be sufficient; free hydrogen ion concentration may not be enough. Titration to different end points may mean different needs for different biological effects. So, if titratable acidity is done, it may be for the wrong end point. Thus, the only general way is to do a Gran titration because that does provide information for an initial pH measurement and because it also provides the data for the total acidity to any end point. It also gives measures of both weak and strong acidity. Moreover, it would not cost much more to do the Gran titration, and it would be supportive of the pH measurements. The group felt that the Gran titration, at least initially, would be worthwhile to have a cross-reference to verify that the pH measurements were correct.

Discussion

Bruce Appel asked if an acid addition strategy to focus only on inorganic acids had been discussed as an alternative to Gran titration. Howard Liljestrand replied that they did talk about adding acid in the extracts to start with an initial concentration. However, they did not discuss the "reverse titration" in the Gran titration, where acids rather than only a base are needed; that was his own view. A clarification was given that the Gran titration, if done properly, does include the initial addition of an acid (such as perchloric acid) to the extract.

Potential data reduction costs of extracting additional information during titration was briefly discussed. Petros Koutrakis noted that they had measured approximately 10,000 values for which they had done an ion balance and found that they were not different by more than 10 to 20%. The Gran titration at each site would be an extra bargain. Bruce Appel's alternate suggestion might even be the best. Liljestrand expressed reservations that the answer by Petros Koutrakis may be restricted to the eastern United States and that at lower, strong-acidity concentrations the titration would be worthwhile. Jed Waldman noted that the hydrogen ion does not contribute that much to the balance, so that the titration, whether end point or Gran, offers additional QA. George Thurston noted that his group did suggest the idea of titration to defined end points. It was not unanimous that the Gran titration wás the only solution.

SUMMARY OF GROUP RECOMMENDATIONS

Robert Stevens gave an overview of all group recommendations. Walter John's group (I) addressed priorities and determined the highest priority item was fine-particle, strong acidity. The other acid aerosol indicators, in order of priority, were: sulfate, ammonium ion, nitrate, ozone, sulfur dioxide, ammonia, nitric acid, nitrous acid, and organic acids. The majority felt that denuders were necessary. They felt that having gas and aerosol data while conducting this intensive study would be valuable (particularly for future resource savings, assessments, and control strategies). Most participants felt that titratable acid was the preferred way of assessing the total strong acidity. Preserving the samples was strongly recommended. The majority view on frequency was that a sample should be taken no less than every third day. The recommended sampling duration was 24 hours. However, during the intensive, shorter sampling times, 12 hours or less should be considered if resources are available.

John Watson's group (II) focused on particle acidity. They felt that the health and research studies should focus on the factors that govern outdoor acidity. Ammonia should be measured and exposure pattern monitoring should also be considered. They identified two types of acidity, pH and titratable. Although pH measurements would probably be adequate, the Gran titration should be accommodated in the early phases of the program. In intensive studies only, sulfate, ozone, sulfur dioxide, ammonia, and fine-particle hydronium ion could be measured. They felt that personal monitoring should be included in initial field studies. They noted that pH measurements can determine both strong and weak acid. They also mentioned the need to measure sulfate, nitrate, and ammonium ions, but that these measurements are not needed to support hydrogen ion compliance monitoring. A filter pack and a denuder probably would be sufficient to gather the hydrogen ion measurements needed. There is a need to measure acidic gases, but not for routine monitoring. Diurnal profiles should be taken, with up to five samples a day, to assess hydrogen ion variability.

William Pierson pointed out that his group (III) had a multitude of species to measure. They felt particle size should be measured to address where the upper cut point should be to minimize alkalinity effects. They wanted a time resolution as short as practicable to assess exposure patterns and a detection limit of 20 nmol of hydrogen ion as a desirable limit for field-study sampling. The need to measure size was repeated in discussing the breath neutralization problem. Members felt that pH would work, as would Gran titration or total titratable acidity. Preservation of the sample was important, and perhaps pH measurements at the sites would be adequate. The group thought ozone should be measured, but acid gases were given a lower priority (to be measured during intensives and only potentially at other times. They recommended measuring sulfates, but not nitrates.

Howard Liljestrand's group (IV) felt that a wide range of gases and particulate measurements should be made to more accurately assess particulate acidity. They felt the issue of the maximum particle size cut point should be examined. Species they felt had the highest priority were hydrogen ion, ammonium ion, sulfate ion, nitrate, nitrous acid, nitric acid, and ammonia. A similar set of extensive measurements should be made in other microenvironments, such as indoors. The frequency of the measurements should be less than 24 hours (perhaps a goal could be set of 18 hours and 6 hours). Gran titrations were recommended by Howard Liljestrand.

A summary of group discussions may be found in Table 1. Each group's recommendations are given for the different issues discussed. No summary is provided in this table for the issues not explicitly discussed by the indicated group.

TABLE 1

SUMMARY OF GROUP DISCUSSIONS ON SELECTION OF ACID AEROSOL

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1. Indicators for Characterization and Exposure Studies

GROUP I

Fine particle strong hydronium ion and fine particle weak hydronium ion by pH and/or titration

Particulate: mass, SO_4^{2-}, NO_3^-, NH_4^+

Gaseous: NH_3, SO_2, NO/NO_2, O_3

Meteorological: wind speed, direction, temperature, relative humidity, pressure, insolation, precipitation

Size-resolved particulate chemistry

Acetic, proprionic, formic and other organic acids

Fine particle elements, organic and elemental carbon, and volatile organic compounds for source apportionment

Indoor/outdoor concentration ratios

Personal exposure monitoring

Aircraft sampling

GROUP II

Particle strong acidity - fine particle size cut

Acid gases and NH_3

Prioritized list:

1. particle acidity
2. SO_4^{2-}
3. NH_4^+
4. NO_3^-
5. O_3

6. SO_2
   NH_3
8. HNO_3 + HONO (HNO_2)
9. organic acids

GROUP III

Particle size - MMD and σ_g at entrance to breathing zone penetrability of 0.3 vs. 0.85 μm may make a difference

Cut at 1 μm or 2.5 μm to avoid alkaline particles

Concentration of strong acid, C

Time of exposure, T

C x T

Time resolution - to be determined by physiology of acute effects and real world exposure assessment

No distinction made between indicators for areas 1-4

GROUP IV

Total acidity and speciation

Particulate: H^+, SO_4^{2-}, NO_3^-, acid fraction at <2.5 μm to <1 μm

Gaseous: HONO (HNO_2), HNO_3, NH_3

Sulfate speciation

Organic acids

Routine monitoring: continuous O_3, NO_x, SO_2, etc.

Table 1 (Cont'd)

2. Indicators for Health Studies

GROUP I
Fine particle strong hydronium ion

GROUP II
See response to area 1

GROUP III
No distinction made between indicators for areas 1-4
See response to area 1

GROUP IV
Total acidity and speciation
See response to area 1

3. Indicators for Indoor Studies

GROUP I
Fine particle strong hydronium ion
NO_2, SO_4^{2-}, HONO, fine particle mass
Frequency of source use

GROUP II
See response to area 1

GROUP III
No distinction made between indicators for areas 1-4
See response to area 1

GROUP IV
Total acidity and speciation
See response to area 1
With measures for factors that lead to systematic biases between indoor/outdoor concentration ratio (e.g., penetration rate, source strengths, etc.)

4. Indicators for Fixed Site Monitoring

GROUP I
All measurements for areas 1 & 2 at fixed sites
Personal exposure monitors for: NO_2, SO_2 (passive) and fine particle mass, strong acidity, ammonia (active)

GROUP II
Minimum set
See response to area 1

GROUP III
No distinction made between indicators for areas 1-4
See response to area 1

GROUP IV
Total acidity and speciation
See response to area 1

Table 1 (Cont'd)

5. pH vs. Titratable Acid

GROUP I
These appear to be equivalent for strong acids (pH < 4)
Additional equivalency tests should be conducted and reported

GROUP II
Could do both
Majority favor titratable, report strong acid
Sample should be kept cold

GROUP III
All existing techniques will work:
- pH is a problem only when ion strength low (may need experiment to assess method of additions)
- Gran
- titratable

New instruments for H_2SO_4 and NH_4HSO_4 (speciated) may render issue moot

GROUP IV
Gran titration preferred; have QA of pH_o and total to any end point
Total acidity and pH_o as a less expensive alternate

6. Need to Measure SO_4^{2-} and NO_3^-

GROUP I
YES for characterization and exposure monitoring
NO for health monitoring

GROUP II
Not discussed

GROUP III
Need to measure SO_4^{2-}
No need to measure NO_3^-

GROUP IV
Measure both, NO_3^- in gas and particulate phases

7. Need to Measure Acid Gases (e.g., HNO_3 , HNO_2 , NH_3)

GROUP I
YES for characterization and exposure monitoring
NO for health monitoring

GROUP II
Not dicussed

GROUP III
Not discussed

GROUP IV
YES for acid gases but with lower priority
HNO_3 should be included
Others should be in some comprehensive stations
No consensus on NH_3 (needed to decide where and when the potential for strong particle acidity exists)

Table 1 (Cont'd)

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8. Measurement Frequency, Duration, and Averaging Time

GROUP I

Two categories:
  (1) characterizaton and exposure monitoring
  (2) health studies
Characterization and exposure monitoring
  duration: 24 hours with intensive sampling of 6 hours, 4 per day
  frequency: daily
  period: each season for 1 year
Health studies: minimum duration: 12 hours, 2 per day
  frequency: every other day

GROUP II

Monitoring for 24 hours, at least every 3 days for 3 years
Shorter-term studies with 12-hour samples, 2 per day for diurnal cycle

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GROUP III

Time resolution to be determined by acute effects and real-world exposure assessment

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GROUP IV

Less than 24 hours needed for peaks (i.e., 18 + 6, where 6 hours at the peak)
Some intensive sampling down to 3-hour intervals every day (but not routinely) to:
  ensure QA - i.e., $\int c\,dt = \bar{c}$(24 hour)
  describe frequency distribution for standards and health effects

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9. Other Areas of Concern

GROUP I

Need to determine optimum size cuts in eastern and western U. S. to minimize alkalinity without eliminating acidity
Weak acids may have an effect, especially in the West
Primary indicator should include fine particle total hydronium as well as fine particle strong hydronium ion, if possible

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GROUP II

Look at available data
Take minimum sample dew point? Heat 1 °C above ambient temperature
Standards reviewed every 5 days

GROUP III

Time resolution needed to evaluate acute health effects and to approach real-world exposure assessment
Detection limit: 20 nmol/m^3 H^+ or 1 μg/m^3 as H_2SO_4
Measure ion balance: at least H^+, NH_4^+, SO_4^{2-}
  NH_4^+ could prove to be a second indicator
Need to do experiments at different cut points (e.g., 1.5-, 2-, and 2.5-μm) to find out what cut point is needed to avoid alkaline material at various locations and also determine σ_g
Preservation of samples also done on site if possible (advantage of doing pH), seal samples, analyze as soon as possible, extract at end of storage period

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GROUP IV

Not discussed

Discussion

John Spengler presented a minority viewpoint. He noted that in Group (IV) an East-West coalition felt that determining the total acidity should be of interest. He noted that Harvard study results indicate that there is a lot of ambient, vapor-phase acidity. Concentrating efforts for the next few years on particle acidity may result in missing urban and even rural influences from vapor-phase acidity. EPA might want to consider a split-system network, one that looks at the strong-particle acidity using a device similar to the one with two impactors, a denuder and filter set setup. At a cost of $2000 to 4000 per site, 100 sites would cost less than $0.5 million to set up. The hydrogen ion or titratable ion can be analyzed for approximately $20 to 50 per sample. Operating these instruments at 100 sites for 200 days a year would cost about $1 million. A larger network is possible using the ADS to obtain other species, e.g., ozone, nitrogen oxide, sulfur dioxide, nephelometers, and meteorological data. If working with an existing operational site was not an option, but a complete site had to be provided, it might cost $50,000 per site. In that case, using two of these systems per region could be considered, for a total of 20 sites that would be rotated every few months. This would cost approximately $1 million in hardware, $0.5 million per year to operate ($25,000 per year for 20 sites), and about $1 million for analysis costs ($200 to 300 per sample). Sampling could be done according to meteorological conditions to assess differences affecting personal exposure. If one sampled for a few months at each site and rotated the sites within regions, the information needed would be obtained. This includes rural/urban differences, species fractions, and regional and climatic differences in total acidity and its component parts. This level of detail will cost more, but if done selectively to answer specific questions it will result in better information for policy decisions a few years from now.

Leonard Newman stated that he was struck by how well aerosol acidity represents total acidity; John Spengler agreed. That is why the design that George Thurston and Morton Lippmann are developing in NYU Medical School may be perfect. If there is strong correlation, aerosol acidity may be an excellent surrogate for total acidity. Newman asked if measuring nitric acid alone was practical instead of aerosol acidity. John Spengler replied that this might not apply to places such as Livermore, CA. Tom Dzubay noted that the system Spengler described was one of two Harvard acid samplers. The other system, presented earlier, demonstrated that apparent hydrogen ion values can be incorrect by as much as 60 to 500%. Petros Koutrakis's work illustrated the need for additional filters to adequately represent the hydrogen ion that has been altered due to other species on the sample. John Spengler replied that Koutrakis's study was done in a controlled chamber. In fact, the correction for ambient air varies from place to place, and, although unknown, sometimes could be as large as the maximum mentioned. Petros Koutrakis said that, after a great deal of thought, he was convinced (by the laboratory data and some initial field data) that it is possible to have ammonium nitrate neutralize significant amounts of sulfuric acid. The dilemma is not knowing exactly how much of a correction has to be made. How could one justify the cost if the correction turns out to be 10-15%. Jed Waldman stated that the point is to obtain an accurate measurement of strong acidity of the particles, and whatever is necessary to do that must be done. Before a monitoring program is even considered, these results should be clearer; the configuration does not need to be decided now.

SECTION 10

DATA QUALITY OBJECTIVES FOR ACID AEROSOL MEASUREMENTS

Dr. Gary Foley of EPA's AREAL discussed data quality objectives (DQOs). He stated that before data are collected, decisions must be made on how the data should be used, i.e., what precision, accuracy, etc., are needed to answer questions. It is a difficult, iterative process. An initial attempt is made to determine DQOs, and they are constantly refined over the life of the program as more information becomes available. DQOs, he said, are poorly understood within EPA even though they have been a mandatory requirement for several years.

Foley presented a generic version of the concept to illustrate a DQO. He listed the following 10 steps in the process of establishing DQOs:

1. Select an environmental need. For this workshop, for example, it is acid aerosols.

2. Define the pollutants or pollutant classes of interest. This is a major issue for this workshop. Hopefully, a consensus will be reached about the priorities for acid particles and acid gases.

3. Define the media and the compartments of the media. Again, several of these items are being discussed during this workshop: ambient air, indoor air, and respired air. Within these media, respirable particles and gases are to be examined.

The first three steps form part of the initial definition. The next steps are as follows:

4. Designate, as specifically as possible, several alternative products. The following items were obtained from the goals of this program: determine the levels to which the human population is exposed, use epidemiology studies, determine an appropriate indicator, develop a federal reference method, and derive a mode of how to determine population exposures.

5. For each of the alternative products, specify the temporal and spatial bounds. This workshop is also considering this item. Alternatives include daily measurements vs. more frequent measurements, spatial coverage, and location of areas for monitoring.

6. For each different monitoring or measurement approach, construct an information flow diagram leading to the product.

Ultimately, the goal is to obtain a risk assessment of acid aerosols. Doing this means providing certain information from the "health side." There are processes for health studies and for obtaining health information. AREAL is trying to provide the population exposure information that must be somewhat compatible with the health information to do the risk assessment. A population exposure estimate is derived from an exposure assessment in monitored cities and combined with an acid model to depict different emissions scenarios and their effects on population exposure. Working backwards, both environmental measurements in cities and data on activity patterns (or activity models) are needed to predict the effects of different activities on exposure to acid aerosols. Finally, some standard measurement or series of measurements is needed to obtain the environmental measurements in the cities.

If the risk assessment shows a need for regulatory action, a monitoring program would ultimately have to be designed to determine compliance with the regulations. A federal reference method and a workshop like this one to decide on the indicator for the federal reference method would also be needed.

Consider a hypothetical case in which one wants to identify the basis for scientific decisions that will be made. The exposure assessment and the health information must be reviewed to determine if there is a risk to health to provide decision makers with an answer. The answer can be divided into categories. Is there a problem everywhere? Only where ammonia is low? Only near major acid sources? Or, is there no problem anywhere? There are often grey areas between these decisions where the information may not be sufficient to determine whether or not a problem exists. For example, it may not be possible to tell if acid aerosol is a problem everywhere or only where ammonia is low. Examples of the next two general steps in the process are:

7. Identify for a specific question the scientific decision process or criteria into which the product will enter (generally, there are three decisions, yes, no, or cannot decide).

8. Test the decision process or criteria with "what if" cases to determine the size of the "cannot determine" range that can be tolerated. Quantify the size of this range or select bounds (upper and lower) for the size of the range.

One of the purposes of the DQO process is to set up a process (with the help of statisticians) to examine the decision process and test it with hypothetical cases to decide how much uncertainty can be tolerated by the decision maker. The decision maker needs to specify this uncertainty in some numerical or probabilistic terms. Working with statisticians and people that understand each step in the process, one works through each pathway of the process back to the basic measurements (epidemiological, exposure in cities, etc.) to determine how much uncertainty can be tolerated in each of these various steps. Trade-offs among the uncertainties in the various steps are also examined, ultimately arriving at the precision and accuracy needed for the methods to make measurements in the cities. The certainty or uncertainty acceptable has then been determined for the standard methods. This is what is meant by the following step:

9. Propagate this range (or upper and lower bounds) back through the flow diagram to determine the bounds on the monitoring or measurement and the trade-offs between compartments.

If the precision and accuracy that are needed cannot be achieved with available money or resources, different factors can be varied: number of sites, number of measurements, frequency of measurements, or precision and accuracy of the equipment. The decision maker can be presented with what can be achieved with available funds, and it can be determined if that is acceptable. If it is not acceptable, the decision maker can help and try to obtain additional funds. Then this process can be repeated. That is:

10. Repeat Steps 4 through 9, adding more information, deleting and/or adding alternatives, and refining the decision process and criteria.

Eventually one should obtain DQOs that can be mutually agreed upon. This is very difficult to achieve at the start of a program. As the project is under way and more data become available, the process should be reiterated, determining DQOs in an evoloving process.

Discussion

Dr. Ruth Allen asked how long would it take to complete an iteration through the process. Gary Foley responded that it would require a great deal of thought, particularly before a shootout is attempted. When asked if the construct included a sensitivity analysis for various control measures that might evolve, Foley responded that he was unsure how to answer the question. The answer was yes and no; those factors that affect precision and accuracy must be known, but exactly what might happen in the way of regulatory decisions need not be known.

To a question about who the decision makers are, Foley responded that they could be people in OAQPS, headquarters, research and development management, or a spectrum from environmental groups and industry; all sorts of decision makers get involved in these processes.

SECTION 11

DESIGN OF COMPARISON STUDIES

REVIEW OF PREVIOUS METHODS COMPARISONS BY CARB

Doug Lawson emphasized that particles responsible for the visibility loss in Los Angeles are acidic. People who make these measurements on submicron aerosol have noted it, and recent data from California studies also show it. There is atmospheric acidity in the particle phase even in Los Angeles.

Lawson discussed the nitric acid shootout at Claremont in 1985, the carbon shootout at Glendora in 1986, and the SCAQS in 1987. It is important to consider the physical layout in designing a study. For example, the inlet of each sampler was kept at a certain elevation above the ground to minimize variations in deposition and other parameters that could affect sampler behavior. Also, it is important to have a platform to serve as a physical barrier to traffic. For the carbon shootout at Glendora, the platform was 150 feet long and had samplers from one end to the other from 30 participating groups. It is also important to use spectroscopic methods if at all possible in a method evaluation study.

Lawson emphasized the need for clearly defining an objective for a study. For the nitrogen shootout, the objective was to validate methods that could be used in the SCAQS to measure nitrogenous pollutants. These included: nitric acid, nitrous acid, ammonia, nitrogen dioxide, and other species.

First, for nitric acid, several continuous methods were to be examined. Among the spectroscopic methods were Fourier transform infrared (FTIR) spectroscopy and tunable diode laser absorption spectroscopy (TDLAS). Also used were a real-time luminal method and a tungstic acid technique (TAT). The following time-integrated methods were used: the annular denuder method, denuder difference method (DDM), denuder tubes, filter packs, and transition flow reactor (TFR). As many different methods that were currently available were tried in addition to spectroscopic techniques. Also, there were spectroscopic methods for nitrous acid, DOAS; for ammonia, FTIR; and for nitrogen dioxide, DOAS and TDLAS. He emphasized the importance of obtaining representative methods and having spectroscopic techniques whenever possible.

Lawson also emphasized the importance of QC and QA; he felt that QA should be done by a third party independent of the investigators. He noted that when the investigators were given spiked Teflon and nylon filters containing nitrate and sulfate, many groups could not analyze the nitrate accurately for several filters. Thus, a significant number of groups that participated in the study had difficulty in obtaining a simple measurement. It is also important to try to challenge the systems that are being used with the material being measured. A nitric acid permeation tube was tried, but it failed. Flow rate calibrations should be done on-site. The basics need to be taken care of. If sampler location on the site is in question, the samplers should be moved around to determine any influence at the site. He emphasized the need for replication by method and within group. It is important to have one group using the same instrument in duplicate and then have others using the same method. Finally, the issue of field blanks and dynamic blanks and how they are handled should be addressed in the data analysis process.

Lawson then discussed and summarized the QA steps used by SCAQS:

1. Review of Standard Operating Procedures (SOPs)
2. Side-by-Side Testing of Samplers
3. Preliminary Systems Audits
4. Field System Audits
5. Performance Audits
6. Intercomparison Studies
7. Documentation

He emphasized the need for side-by-side testing of samplers to determine the precision for routine monitoring. Data cannot be used without knowing its precision. Field audits of the samplers must be done to ensure that the flow rates and other factors are being measured appropriately. He noted that performance audits should be done in the field for all instruments without exception.

Lawson emphasized that when traceability standards are not available, simple intercomparisons or methods evaluations should be used. This may be possible for a field study or a shootout for particulate acidity. He suggested the need for a test to challenge investigators by using ions on filters to try to establish some type of equivalency among methods.

Finally, Lawson emphasized the need for documentation as part of QA. He noted that it is an expensive step and disliked by everyone, but essential to ensure integrity of the data. He then gave some examples of QA from SCAQS. He showed results for the hydrocarbon comparison indicating less than a 10% uncertainty for speciated hydrocarbon measurements; this was the first time it had been done for hydrocarbon measurements. He pointed out that although some of these QA items may seem trivial, they are necessary. He illustrated the point by citing examples of incidents during SCAQS.

Routine calibration audits by CARB for routine analyzers (for ozone, carbon monoxide, nitrogen dioxide, sulfuric dioxide, total hydrocarbons, etc.) showed deviations of 25-80% in some instances. These results were for very prominent research groups and yet they had difficulty with basic measurements. The results have to be documented and it must be done in the field to ensure the integrity of the data.

Lawson next discussed the issue of concentration vs. sampling time. It is an issue that needs to be addressed in designing the study, because if short sampling times are used higher concentrations are found. He presented some data for gaseous species to estimate the difference. For short sampling periods of 5 minutes or less, there is a factor of four difference in concentration compared to a 24-hour average.

Lawson noted that he was pleased to see the Harvard data presented earlier showing the importance of gas-phase acidity. He noted that Los Angeles is the only place in the United States with information on organic acids and that in Los Angeles the dominant part of acidity is due to organic acids during a substantial part of the day. The nature of atmospheric acidity for other parts of the country is speculative, but is something that should be addressed.

Lawson presented a wish list for field studies that included the following:

1. Quality Assurance - make sure it is done properly
   Review SOPs including error analysis
   Systems Audits
   Performance Audits
   Method Precision/Accuracy
   Laboratory Precision/Accuracy
   Intercomparison Studies

2. Deadline for Submittal of Final Data

3. Publish Results and Provide Symposium

Lawson also discussed some thoughts about an atmospheric acidity study. For health effects reasons, it is important to measure gas- and particle-phase acidity. Gas-phase acidity may exceed particle-phase acidity. Sampling time is important to gain insights on formation and fate of various species. Measure as many species as economically feasible, keeping diminishing returns in mind, and focus on copollutants. If fortunate, a study will be designed that will be of use not only to health effects researchers, but also to chemists, modelers, and others.

He emphasized that because of the emotional ties of groups to their own samplers, it is important that an independent third party conduct the study. He cited examples of shootouts where a group had opinions on how data are to be interpreted after the fact and it caused problems among the investigators when interpreting the data. In one case, corrected data were submitted after the deadline and it is unclear how to resolve the discrepancy. It is necessary to have a clear protocol outlined as the study is designed.

Discussion

Jed Waldman asked who the final arbiter should be. If three agree and line up and two agree and line up, which group is right? Doug Lawson answered that it depends on the species. When looking at particle acidity, one does not have the advantage of spectroscopic methods to help. Such methods are a help with nitric acid and, to some extent, ammonia.

Otherwise, it is difficult to answer that question. If one could use something like spectroscopy that does not use plumbing and if one could confirm the measurement by using two such techniques with independent calibrations, then one could have greater confidence. Particle-phase measurements would be difficult.

REVIEW OF PREVIOUS METHODS COMPARISON IN ITALY

Dr. Ivo Allegrini, of the Instituto sull'Inquinamento Atmosferico del Consiglio Nazionale delle Ricerche, spoke about the intercomparison run in Rome several months ago. He noted that there are many places in Europe where the amount of acid aerosols is so large as to be a health hazard to European citizens. He gave several reasons for conducting the intercomparison, which included political and technical reasons. The political reason was the opportunity to bring together scientists from many countries. The technical reasons were (1) to review the state of the art for measuring atmospheric pollution, (2) to select from among the many methods available the best ones for use in the field, and (3) to focus attention on the measurement of two important compounds in acid deposition and photochemical pollution, namely nitric acid and particulate nitrates.

Allegrini then discussed the conduct of the intercomparison at a site near Rome. Many instruments used for auxiliary measurements of individual components were located in a pilot station at the site. Persons were allowed at the sampling site only during intervals between sampling. There were many different instruments and samplers--filter packs, annular denuders, cylindrical denuders, etc. In the pilot station were such instruments as: a PAN analyzer (specifically developed within the Institute), luminal machine for nitrogen dioxide, a beta-ray gauge, and other instruments to measure meteorological parameters, sulfur dioxide, nitrous acid, formaldehyde, ammonia, hydrogen peroxide, ozone, PAN, nitrogen dioxide, and ammonium, nitrate, and sulfate in particulate matter. In addition, the nitrate radical in the atmosphere was measured by using DOAS. All participants used their own method for the measurement of nitric acid in the gas phase and nitrates in particulate matter.

There were 50 participants: 40 from individual countries and 10 from the National Council of Research. The 50 participants consisted of 20 different groups from 14 different countries. The European Economic Commission paid for travel expenses and accommodations, while the National Council of Research paid expenses for general organization and analytical work.

The analyses were done by the Institute, thus avoiding the issue of QA and QC among several laboratories. As a consequence, more than 4000 analyses were done using IC.

A low-pressure permeation source was used for the field calibration of instruments measuring nitric acid. A computer-controlled device was used to control flow rate and sampling volume for the instruments used by the other participants. Among the instruments used to measure nitric acid and nitrates in particulate matter were a thermal denuder, an annular rotating (wet) denuder, a Berner impactor, cylindrical denuders, filter packs, and annular denuders. The thermal denuder is an annular denuder coated with magnesium sulfate. By keeping the tube at different temperatures, one can measure the concentration of nitric acid and particulate nitrate about every 15 minutes. The annular rotating wet denuder is a semiautomatic machine that provides measurements every 15 minutes for nitric acid, ammonia, hydrogen peroxide, etc.

Allegrini next discussed preliminary results from the intercomparison including some data showing a problem in a comparison of the annular denuder method and the filter pack. The filter pack is used in a network consisting of 70 stations throughout Europe. The intercomparison lasted 5 days. Each day was divided into four periods (8 a.m. to noon; noon to 4 p.m.; 4 p.m. to 8 p.m.; and 8 p.m. to 8 a.m.). The concentration of nitric acid was very low during the first day. Then meteorological conditions created a buildup of nitric acid to about 10 $\mu g/m^3$. Since the sampling site was located about 30-35 km northeast of the center of Rome, it was away from most emission points and traffic. There was reasonable correlation for nitric acid for the filter packs with the annular denuders ($r = 0.93$, $m = 1.28$). Similarly, nitrates in particulate matter seemed reasonable. However, during the intercomparison, collocated samplers were also run for 24 hours (8 p.m. to 8 p.m.) because at night there is a buildup of nitrates in particulate matter.

One test of consistency is to compare the average of the four daily measurements with the 24-hour period. Consistent results are seen for nitric acid, nitrates, and the sum of the two for the denuder measurements. However, that is not the case for the filter packs where good consistency is obtained for the sum of the two, but not for each of the individual species. In comparing the filter pack and denuder, a consistent sum is found for the two species, but not for the ratio. The denuder offers an upper limit for the measurement of nitric acid and a lower limit for the measurement of nitrates. Therefore, the ratio of nitric acid/nitrate should be an upper limit. Certainly, if another method gives a higher value than the value from the denuder, something is wrong. In this case, there is a volatilization of ammonium nitrates from the filter. The nitric acid average concentration is fairly good during the afternoon and overnight, but not during the day because in the morning there is a rapid drop in relative humidity and an increase in the ambient temperature. The situation for nitrates is just the opposite. However, the sum is consistent, which is a very good indication that the analytical work was done well.

When examining the difference between the nitric acid as measured by the filter pack and denuder and also the particulate nitrates as measured by the two methods, what is gained on the nitric acid side is lost on the nitrate side. In the annular denuder method, the evolved nitrates are measured because there is a nylon filter behind the Teflon filter for the collection of particulate matter. The maximum amount of evolved nitrate occurs during the period 8 a.m. to noon. In the regression analysis of the sum, one can see that the sum is well correlated ($r = 0.97$, $m = 1.1$). However, something is wrong when the correlation for both nitric acid and nitrates is 0.9, because the correlation for the sum cannot be greater than the correlation of its parts.

SECTION 12

DESIGN OF LABORATORY AND FIELD METHODS TESTING AND COMPARISON PROGRAM - GROUP DISCUSSIONS

At the end of the second day of the workshop, participants were again divided into the same four working groups. Each group met and made recommendations about the issues listed below that address designing a program for laboratory and field methods testing and comparison:

- Review of the objectives
- Participants
- Species to be measured
- Measurements: frequency, duration, and averaging time
- Data analysis and reporting
- QA/QC
- Site selection and time of tests
- Testing: laboratory vs. field
- Reference methods

After discussing these issues, participants convened the following morning to hear summaries of each group's recommendations. Then an overview of group recommendations was given, followed by further discussion.

GROUP I

Objectives

John Watson reported on the recommendations of Group I. He discussed the issues in the order they were listed on the agenda. The group interpreted "objectives" to mean "objectives of a testing and comparison program" and listed four:

1. Resolve outstanding sampling and analysis issues common to many measurement methods.
2. Establish equivalency among laboratory analytical procedures with respect to sample handling, extractions, storage, and analysis.

3. Establish relationships among measurements from existing measurement networks.

4. Determine equivalency of methods to measure fine-particle strong hydronium ion and determine causes of differences among measurement methods.

The group felt that one advantage of previous intercomparisons has been the opportunity to compare measurements from different networks operated in different areas. These results could be evaluated, perhaps combining data and drawing additional inferences from them. The group said a testing and comparison program would be useful.

Participants

The group agreed that, in general, the participants should be the operators of current long-term acid aerosol measurement networks. The following groups were listed:

- New York University Medical School
- Robert Wood Johnson Medical School
- Harvard University
- California Air Resources Board

The ones identified were those already taking long-term, as opposed to episodic measurements; others may be identified later. The group felt that a second part of the measurement comparison is the identification of real-time measurements. The two methods identified for continuous measurement of acid aerosol were IR measurements and flame photometric detection.

Species

The species to be measured were divided into two categories. One category was the "evaluation" measure, i.e., the measure used to compare the different measurement methods among the different networks. The group had defined it earlier as fine-particle strong hydronium ion. A provision for both a pH and a titration measurement was considered necessary because there is a certain degree of operational definition to this measure. These measurements would be independent of the sampling method. The second category was the "explanation" measure. The group felt several explanation measures were needed because one of the group's objectives was to explain (rather than note) the differences observed. This requires other supporting measurements that should include the following:

Particulate	Gaseous	Meteorological
sulfate	nitric acid	wind speed, direction
nitrate	sulfur dioxide	relative humidity
ammonium	ozone	temperature, pressure

Chemically speciated, fine-particle distribution should also be measured.

Measurements

An important issue was the extent to which soil particles might neutralize the acid, given the different size cuts in the measurement methods. Thus, size distribution data were felt to be necessary. For the measurement frequency, duration, and averaging time, Group I felt that a 10- to 20-day test would be adequate. Because many current networks are taking 24-hour samples, the group included this as part of the test. There would be three identical samplers from each network. The first one would be used to take the 24-hour sample, and the network laboratory would be used for the analysis. The second sampler would alternate between a 24-hour sample and the shortest time period possible. The purpose is twofold: (1) to obtain a collocated precision (a side-by-side precision with the first sampler) and (2) to determine the extent to which a long-term, integrated sample would have neutralization from combining high and low acidity material over a diurnal cycle. The third sampler would consist of the normal network operations (day/night, 12-hour, etc.), with analysis by pH and titration for fine-particle, strong hydronium ion in the organizer laboratory. These three sampling systems would allow the different objectives to be addressed.

Data Analysis and Reporting

Data analysis and reporting were divided into three areas: documentation reporting, actual data reporting, and data interpretation. Group I felt it was important that every group participating submit its SOPs to be reviewed by the independent organizer. The following would also to be submitted: a description of the monitor and parts list, inlet penetration curves (if available), copies of station logs taken during the test, formulas used to calculate precision and minimum detectable limits (MDLs), and the method for calculating volume. It was noted that the method for calculating the volume and the method for normalizing it to certain temperatures and pressures can affect what is observed, especially when mass flow controllers are used instead of volumetric flowmeters.

The group felt the following data should be reported: testing results, blank and replicate analyses, precision, MDLs, concentrations in predefined fractions (which the group did not define), and averaging times. The group also felt that comparing the same quantities was important. Moreover, if there is a corrected and an uncorrected value for a parameter, both should be reported in the data base.

Because no method exists that could be called a reference at this time, the use of benchmarks was discussed instead. The group initially considered using a particular sample or some conglomerate (such as the average of all results) as a benchmark, but rejected this idea because the benchmark would not necessarily be correct. Instead, Group I favored paired comparisons. Initial data interpretation should be prepared by the organizing entity and distributed to the participants with no oral conclusions released (to minimize unsubstantiated conclusions). Then participants would be able to comment on this master interpretation, resolve observed differences in a series of more detailed papers, and publicly present the results at a meeting or in a journal. The group felt it important to define the process at the beginning and have the participants agree to it.

QA/QC

Five essential items for QA/QC were listed by the group: (1) conduct acceptance testing of substrates by the organizer well in advance of sampling; (2) review SOPs and a summary of performance tests (to allow the preparation of a table of performance test measures and frequencies); (3) use a primary flow rate standard on site (against which all transfer standards would be referenced); (4) conduct independent flow and elapsed time audits at the beginning and end of the field studies; and (5) require reference liquids with known concentrations to be analyzed by the laboratories.

Site Selection and Time of Tests

Site selection and time of tests were given a prioritized rating based on resources. The eastern United States was felt to be more important because of a higher concentration of acid there. One could use current data bases to determine locations likely to have good variability in acidity, and then logistics should be considered. Pennsylvania State University was mentioned as a potential site because of existing collocated monitors. Although a summer study should have the highest priority, having both a summer and winter study would be preferable. If resources allowed, tests in the western United States would be worthwhile.

Testing

Group I felt that testing should be a four-step process, especially including laboratory testing. Laboratory tests should be initiated first to resolve common uncertainties, including the need to keep samples cold and determine the extent of filter artifacts. Whenever possible, uncertainties should be recorded, the information compiled, and results documented by the independent party. The remaining issues would be subject to tests conducted by the independent party, and all results would be distributed.

The second step is a chemical laboratory test to meet the group's second objective. These tests would include three types of samples: (1) liquid standards to test analytical instrument calibration, (2) impregnated filters with known deposits of species of interest, and (3) samples with species of interest and potential interferents.

The third step is a field test, with possible laboratory components such as the use of a sulfuric acid aerosol mist generator, if one could be developed. The fourth step is follow-up laboratory sampling. Actual laboratory sampling of mists of acidic particles would be better done after the experiment to resolve differences identified in the field test.

Reference Methods

Group I changed "reference methods" to "benchmarks" because it thought the term reference was somewhat premature. The group concluded that no current method can be accepted as a reference. Primary standards for fine-particle, strong hydronium ion are needed. These studies must be conducted with care because differences among the methods are certain to be observed. The goal is not to identify a given method as right or wrong, but to determine why there are a differences.

GROUP II

Objectives

Walter John reported that Group II felt that a comparison study is necessary and that the primary objective is to develop a method for monitoring acid particles in an EPA nationwide network. However, the group recommended that the comparison study start in a controlled atmosphere or chamber. There are so many variables in the ambient air that it would be too difficult to determine the reasons for differences among samplers. After the chamber tests, the final test would be done in the atmosphere to look at unanticipated, real-world problems.

The group gave an example of how the chamber tests would work. The study would begin with pure acid sulfate particles and then other possible interfering pollutants would be added successively. A majority of the group felt as a minimum requirement the sampler should be able to measure acid particles. A minority said that the sampler should 4also be capable of measuring nitric acid. Tests would be performed on a stripped-down model of the sampler to be used in nationwide routine monitoring, and not an advanced research version. The group liked the idea used in a European intercomparison of sending all the samples to a central laboratory for analysis. Such a comparison would test the sampling method and not the analytical method. The group recognized that tests of the laboratory analysis techniques would be necessary, but felt they should be conducted separately from the tests of the samplers. They also felt that the laboratory analysis method might have to be modified to accommodate the sample load generated by a monitoring network.

Participants

The group felt that EPA should invite as participants those researchers with the most advanced, currently operating systems. Some of the samplers listed were:

1. The Harvard ADS

2. The Waldman version of the ADS (where the back-up filter and impactor are different and the sample is stored dry, as opposed to the Harvard method where the sample is extracted and the wet solution is retained)

3. The Lippmann-Thurston sampler with a honeycomb denuder (which is not suitable for extraction and has a different type of impactor)

4. Newman's suggestion of a sampler consisting of a denuder, quartz filters impregnated with sodium chloride for acid gases and carbonate for sulfur dioxide, etc.

5. Filter packs - on a 1-hour basis they may afford a simple, cost-effective solution

6. The transition flow reactor (possibly)

Species

All methods would be run in duplicate, in a "single-elimination tournament." It would start with simple acid particles. Those methods that pass that test would advance to the next test and so on. The final "survivors" of the elimination process be subject to field testing. The species would include: (1) fine-particle acid sulfate (generated in the chamber with controlled particle sizes that could be varied, and concentrations would be changed to span the range seen in ambient air), (2) interfering species (although the total number of possible interfering species should be limited to have a manageable matrix of combinations), and (3) ambient particles with condensed acid. The chamber could be monitored with a FPD for sulfur. Aerosol monitors such as optical detectors and gas monitors such as FTIR could be used. If available, Johnson's IAA instrument would be desirable. This instrument offers promise in serving as a reference method, although one would have to be careful about the inlet design.

Remaining Issues

The testing protocol would be drawn up with the active participation of everyone involved to ensure preagreement about what should be done. EPA should offer to supply operators. The participants would set up their systems and let EPA operators run them.

The protocol for the final field test would be adequately designed by following examples including CARB and SCAQS. The group did not recommend that EPA undertake a multiple-city study because it felt that data from the current multiple-city studies (such as Harvard's and others) could be used. The proposed validation test would, in effect, validate those samplers so that the data could be used. Based on the results of the tests, however, EPA might add whatever is necessary to these city networks to complete the sampling. The chamber studies might also provide data that are relevant to ongoing health effects studies.

GROUP III

Testing

William Pierson reported that the majority thought that the intercomparison should be done in three stages. First, an intercomparison should be done on sulfuric acid-doped filters sent to the various laboratories at a series of concentrations. Second, a chamber-generated laboratory study should be done on sulfuric acid at various concentrations and other conditions. Third, a field study should be done. Some felt that the third step would be justified only if the preceding two steps are performed. The field study would involve identifying a standard sampling inlet size to eliminate size as a factor in the comparison. Each group would have a second sampler with a nonstandard inlet (its own inlet instead) to test inlet problems. A continuous total particulate sulfur instrument would be run concurrently. Sometimes both samplers would be located on the standard inlet, and at other times both would be on the nonstandard inlet. Alternately, a third sampler is needed to provide information about reproducibility (collocated sampler precision).

Species

Group III felt there should be a short- vs. long-term sampling comparison and that the species to measure were:

1. Strong acid in the fine-particle phase (with agreed cut size)
2. Size distribution of the strong particle acidity (hydrogen ion)
3. Ancillary measurements on the gross material and on the size-separated stages for ammonium ion, sulfate, nitrate, and gaseous measurements for ammonia, nitric acid, sulfur dioxide, ozone, and
4. Fine mass and nitrogen dioxide (with lower priority).

The group felt that after completion of each of the above phases, results should be distributed to the participants before advancing to the next phase. Sufficient time should be provided for the material to be reviewed between phases.

Some felt that the field intercomparison should be done twice in the summertime: once at a pure, sulfuric acid-type site (such as Parsons, WV, or Allegheny, PA) and second at a dirty site with high levels of ammonium nitrate, sulfuric acid, and nitric acid part of the time (such as Zanesville, OH). The group noted that the field intercomparison probably cannot be done before the summer of 1990 because filter and chamber tests must be done first. The second intercomparison would follow the first.

Data Analysis and Reporting

The group agreed that data should be submitted to a third party to analyze and report. A simple reporting form should be used that would be designed, agreed upon, and distributed. All participants should agree on confidentiality and then distribution at the appropriate time.

Measurements

Group III felt that 2 weeks at the first site should be allowed for the duration of the experiment to ensure sampling during an episode. For sampling duration, 6-hour samples should be taken, if possible, without skipping intervals. Samples could be taken more frequently, but the shorter times must be aggregated to permit comparison with the 6-hour samples. Some methods might not be able to achieve 6-hour time resolution (12 to 24 hours, for example). However, these methods could be included if they serve as a useful diagnostic tool of the work of others. The group felt that present technology could be improved significantly. It did not want the focus on the intercomparison to hinder efforts to develop improved instrumentation, such as a continuous monitor that could quantitate sulfuric acid and ammonium bisulfate separately.

GROUP IV

Objectives

Howard Liljestrand reported that Group IV identified two main objectives and then discussed other items. The two main objectives were:

1. Evaluate existing methods for particulate acidity with respect to artifacts, evaporative losses, biases, recovery, reproducibility, and practical aspects.

2. Determine limits of detection and precision over the range of ambient levels, with review of error propagation in the field values (with the ultimate goal of identifying the limiting factors in these techniques).

Among the other items discussed were:

3. Establish a small, technical steering committee to handle many of the pragmatic details. At the onset, they should evaluate the previous shootouts, learn from their practical problems, set up the overall design, and then handle basic details.

4. Intercompare methods to provide a common base for historical data bases; represent historical methods at a shootout to make these intercomparisons possible.

5. Design tests to identify fundamental errors or limitations (e.g., stability of ammonium ion, nitrate, and hydrogen ion); i.e., determine if values are correct and not just approximate.

Participants

The group was not concerned about participants because invited groups would come; the question should be how to limit the possible participants to obtain a manageable number. At the onset, the group wanted to include everyone to obtain intercomparisons for historical data bases. The group wanted the following instruments represented:

- Filter pack

- Annular denuder for ammonia, impactor size cut, and filter pack

- Annular denuder for nitric acid and ammonia, impactor size cut, and filter pack

- Short-term dichotomous samplers, impactor or cyclone at the top with Teflon or quartz filter media (taking short enough samples to eliminate blow-off losses and ensure equilibrium with gases)

- Spectroscopic-based and continuous methods (IAA)

Species

Group IV wanted all species necessary for mass and charge balances to be measured and felt that the Italian intercomparison was a good example. Thus, even if analyzers would not normally report certain values, the group wanted that information to investigate where the material was deposited up in an instrument. By ensuring that all species were included in the mass and charge balances, all participants could compare totals found.

Measurements

The group felt that some details about measurement frequency, duration, and averaging times should be defined by the technical steering committee. However, such details should be defined ahead of time and include replicates (at 24 hours). At the minimum, day/night studies were desired to test the effects of temperature, and short-term sampling was desired to describe the diurnal patterns and to ensure the techniques could measure the range of concentrations in the ambient atmosphere. A practical answer might be a 6 + 6 + 12-hour sampling pattern, where the 6-hour periods would come at the expected peaks and the 12 hours would be at night. The sampling regime would add up to 24 hours to allow for a longer-term mass balance comparison. Six hours would also allow groups to stay within their detection limits under varied conditions. The group discussed a field test lasting about 10 days.

Data Analysis and Reporting

Many of the group's thoughts about data analysis and reporting were expressed by others. However, the group felt all the participants should agree ahead of time to the following:

1. Set a due date for data to be reported.

2. Review computer-entered data after entry into a common computer data base and prior to detailed analysis.

3. Specify the units to be used.

4. Participate in a symposium afterwards to discuss results and lead to peer- reviewed publication(s).
5. Use of an independent third-party evaluator (one without a vested interest) to write reports and provide direction.

QA/QC

Many of the group recommendations for QA/QC were mentioned before and included the following:

- Identification, implementation, and reporting of QC used by group/method

- SOPs with error propagation

- Group replicates for field precision
- Charge balance for hydrogen ion
- Mass balances for reduced nitrogen, nitrate, and sulfur species

Other recommendations not reported by previous groups include:

- Monitor fine particulate acidity-to-sulfate ratio
- Trace absolute sulfate concentrations (one of the few conservative species) as a flow check

In addition, Group IV also wanted the following:

- Flow audits both before and during the field study (both internal and external QA and QC)
- Blind, spiked filters (positive controls) as both field and laboratory checks
- QA laboratory to check standards prior to testing to validate any stored or distributed materials
- An aerosol delivery system to provide known concentrations in the field (standard additions) to spike the ambient concentrations to increase concentrations or provide interferences

Site Selection and Time of Tests

For site selection and time of tests, the group discussed two options (with the first option having greater interest from the group). The first option was a field test (in the East) to identify field problems--once in the summer (July/August) and once in the winter; and include a laboratory shootout (at Research Triangle Park) to allow controlled generation of a range of conditions. If the first option was not possible, then the second option was to select two sites and two seasons (minimum); if hydrogen ion with sulfate is emphasized, West Coast testing is not required.

The group felt that it would probably be less expensive and more valuable to do one field test and the laboratory shootout. If only the field test were done, materials would need to be generated to spike into the ambient air to investigate what artifact and recovery problems existed.

Testing

On the merits of laboratory vs. field testing, Group IV was concerned about whether the delivery system for a laboratory study could provide sufficient flow of standard materials to supply replicate instruments for several groups (a minor problem). Again, the group did feel that field testing was required as a practical test.

Reference Methods

As reference materials, the group wanted to be able to generate standards of known particle size for ammonium sulfate, ammonium bisulfate, and sulfuric acid. These standards would be used to challenge the samplers to see if they could recover the materials in the right places. An option that was considered briefly was to use radioactively labelled materials to better identify where species were deposited. The group felt that there is no standard measurement instrument at present, but that some kind of continuous measurement should be used, even if it is not a reference method. One possibility was the IAA for continuous speciation.

Discussion

Two group members added comments. Dr. Ron Bradow noted that the existing data were not only for use in shootouts, but for determining the range of acidity, copollutants, etc., in designing studies. George Thurston discussed the possibility of using weather forecasting to decide when to start the study. Participants might set up monitors, leave, and return to operate instruments when a forecast predicts an episode.

SUMMARY OF GROUP RECOMMENDATIONS

Dr. Kenneth Knapp summarized the recommendations of all the groups. Most groups agreed on many of the areas, especially regarding laboratory design, field methods testing, and a comparison program.

All groups agreed that the main objective was to evaluate methods for their capability of measuring strong acid aerosols. Other objectives mentioned were determining the different parameters influencing measurement methods, determining sample stability, and performing error analysis. All groups agreed that there should be a methods comparison study. Knapp interpreted this to mean (in part, based on his group's input) that without preliminary laboratory studies, field tests would likely not be worthwhile.

Timing was not discussed in great detail except in Group III. Beginning field tests without the laboratory work seems impractical, and the laboratory work will probably not be completed this year. Thus, the first opportunity for field testing during optimal conditions (i.e., the summer) would be in 1990. Groups II and IV discussed predicting when to sample. At least two groups discussed the use of historical data to select the times. Based on this, an episode could be expected every 5 to 7 days for some of the recommended sites. However, as was mentioned earlier, Los Angeles had major episodes approximately every 4 or 5 days for 15 consecutive summers; yet once one study was under way, no episodes occurred for weeks.

Most groups agreed that ancillary measurements should be taken. One issue emphasized by Group III and alluded to by other groups is that these measurements should not be the focus of the methods comparison. If measurements were done twice, two different answers would probably be obtained; thus, selection of only one group to do most of the ancillary methods might be better.

Most groups agreed on the frequency of measurement and that instruments should not be pushed to their limits. Six hours was felt to be a reasonable sampling time, but longer or shorter sampling times were acceptable as long as they allowed comparison with the primary sampling period. Group III felt strongly that a 24-hour sampling period for the comparison would not answer some of the major questions likely to arise because it is much easier to add sampling periods together than to separate them.

All groups agreed on approximately 10 days for field sampling. Most groups agreed on the need for a protocol to be established beforehand. They also felt that participants should submit documentation including SOPs and QA plans. Several groups stressed that without proper QA/QC, the study would be useless. Everybody agreed that the laboratories must be tested with standards. One group suggested using a central laboratory to eliminate this need, but this also would eliminate the possibility of evaluating the analytical techniques used by various groups. Although it would be difficult to find a suitable laboratory, the idea of hiring a central laboratory should remain an option.

Another issue that was discussed extensively was whether to use pH, end point titration, Gran titration, or other measurements. Many felt this issue needed further evaluation; others felt the need to have enough information to perform ion and mass balances.

Knapp felt it was the consensus of all four groups that if only one field study could be performed, it should be done in the summer in the eastern United States. If more money were available, the West Coast would also be an option. Many felt that some type of chamber study would be desirable. Some felt it might be possible in the field; others felt it should be another phase of the laboratory work. Knapp felt that Group IV's remarks about standards were very important, particularly those comments about how and where to set a size cut.

A summary of group discussions appears in Table 2. Each group's recommendations are given for the different issues discussed. Some groups did not explicitly address certain issues.

Discussion

Tom Dzubay noted that Group IV had discussed the question of whether the sampling time should be 6, 12, or 24 hours. Some felt that four 6-hour samples might not table 2 add up to a single 24-hour sample due to artifacts. To solve that problem, the group suggested having simultaneous sampling–one sampler running for 24 hours and the other samplers running for shorter periods. Ken Knapp added that William Pierson had mentioned it for Group III. Group III also noted that if a method is to be tested, more than one sampler is needed. The group did not produce a complete protocol, but felt that a minimum of three samplers would probably be desirable.

TABLE 2

SUMMARY OF GROUP DISCUSSIONS ON DESIGN OF LABORATORY AND FIELD TESTING PROGRAMS

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1. Review Objectives

GROUP I

- Resolve outstanding sampling and analysis issues common to many measurement methods
- Establish equivalency among laboratory analytical procedures with respect to sample handling, extraction, storage, and analysis
- Establish relationships between measurements from existing measurement networks
- Determine equivalency of methods to measure fine particle strong hydronium ion and determine causes of differences among measurement methods

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GROUP II

- Primary objective is to develop a method for monitoring acid particles in an EPA network

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GROUP III

- Not discussed

GROUP IV

- Evaluate existing methods to measure acidic particles with respect to artifacts, evaporative losses, biases, recovery, reproducibility, etc.
- Determine limits of detection and precision over range of ambient levels with review of error propogation in a field measurement (for identification of limiting factors)
- Review previous shootouts by a small Technical Steering Committee to fill in programmatic details and QA
- Current intercomparison to provide commonality to historical data bases
- Design testing to identify fundamental errors or limitations (e.g., stability of NH_4^+, NO_3^-, H^+ on filters and in field extracts)

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2. Participants

GROUP I

- Operators of long-term acid aerosol measurement networks (e.g., New York University Medical School, Robert Wood Johnson Medical School, Harvard, California Air Resources Board, etc.)
- New technology real-time measurements (e.g., IR, FPD)

GROUP II

- EPA limits invitations to most developed, cost-effective samplers
  - Harvard annular denuder
  - Waldman - back-up filter different, impactor different, samples stored dry
  - Lippmann/Thurston - honeycomb denuder (no extraction), impactor different
  - Newman - denuder, quartz filter, NaCl - acid gases, carbonate - SO_2
  - Filter packs - Canadian and others
  - Transition flow reactor (maybe)

Table 2 (Cont'd)

GROUP III

- Not discussed

GROUP IV

- Current operators of ME-35/OEN/dichotomous sampling networks
- Filter pack
- Annular denuder for NH_3, impactor size cut, filter pack
- Annular denuder for HNO_3 and NH_3, impactor size cut, filter pack
- Short-term dichot - impactor/cyclone with Teflon/quartz filter
- Spectroscopic-based method - infrared aerosol analyzer

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3. Species to be Measured

GROUP I

- Evaluation measure: fine-particle strong hydronium ion
  - use pH and Gran titration, strong and weak acid end points
- Explanation measures: chemically speciated fine particle distribution
  - particulate: SO_4^{2-}, NO_3^-, NH_4^+
  - gases: HNO_3, SO_2, O_3
  - meteorology: wind speed, direction, relative humidity, temperature, pressure

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GROUP II

- For "single-elimination tournament:"
  - go from pure species to increasing complexity
  - fine particle acid SO_4^{2-} at start
  - controlled, varied particle size
  - range of concentrations based on ambient values
  - limited by practical considerations (size of matrix)
  - ambient particles with condensed acid at end
- Majority wanted acid particle sampler only (but able to withstand interferences)
- Minority wanted sampler capable of sampling HNO_3
- Tests would be on simple versions suitable for routine monitoring
- Laboratory analyses done in central laboratory
- Test would include analysis components for acid, NO_3^-, NO_2^-, NH_4, etc.
- Method suitable for mass production

GROUP III

- Strong acid in fine-particle phase (but need to agree on a cut size)
- Size distribution of H^+
- Ancillary measurements for NH_4^+, SO_4^{2-}, NO_3^-, NH_3, HNO_3, SO_2, O_3
- Fine mass and NO_2

GROUP IV

- All necessary for mass and charge balances: NH_3, NH_4^+, SO_4^{2-}, NO_3^-, HNO_3, etc.

Table 2 (Cont'd)

4. Measurement Frequency, Duration, and Averaging Time

GROUP I

Three of each type of sampler
10- to 20-day test
Sampler 1: 24-hour sample; analysis in network laboratory
Sampler 2: alternate every other day; 24 hours and diurnal (4 to 6 hours or less if detection limit permits); analysis in network laboratory
Sampler 3: normal network sampling duration; analysis by pH and titration in organizer laboratory

GROUP II

Not discussed

GROUP III

2-weeks duration at first site to catch episode
6-hour samples, if possible, without skipping intervals
Let persons sample more frequently if they wish, but done in a way to permit comparison with 6-hour samples
Some methods with sampling times longer than 6 hours could be included for diagnostic purposes

GROUP IV

Some details left to Technical Steering Committee
Define specifics ahead of time
Test temperature effects (day/night)
Test ability to measure diurnal patterns of concentration
Parallel 24 hours and 6 + 6 + 12 hours (with 6 hour at peaks) sampling for mass balance

5. Data Analysis and Reporting

GROUP I

Document reporting:
- SOPs, description of monitor and parts list, inlet penetration curve, station logs, precision and MDL formulas, and volume calculation

Data reporting:
- Acceptance testing results, blanks and replicates, precision and MDLs, concentrations in predefined fractions, and averaging times

Data interpretation:
- No benchmark (paired comparison), unbiased party prepares report and distributes to participants (no oral conclusions), individual analyses by investigators to resolve differences, and public presentaion of results

GROUP II

Not discussed

Table 2 (Cont'd)

GROUP III

- Submit data to third party to analyze and report
- Simple reporting form should be designed, agreed upon, and distributed
- All participants agree on release of data at appropriate time and on confidentiality before that time

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GROUP IV

- Memorandum of understanding with
  - due date for data reporting
  - review of data after computer entry
  - uniform units specified
  - symposium to discuss results and publication
  - independent third party evaluation

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6. QA/QC

GROUP I

- Acceptance testing of substrates by organizer
- SOP review and performance test summary
- Primary flow rate standard on-site
- Flow and elapsed time audits at beginning and end of field studies
- Reference liquids with samples sent to laboratories

GROUP II

- Testing protocol agreed to by participants
- Protocol patterned after CARB SCAQS, etc.
- Offer use of EPA-designated operators
- All methods in duplicate

GROUP III

- Common inlet for everyone to sample from (same cutoff)
- Second sampler without common inlet in each case to test inlet problems
- Part of the time both samplers would be on common inlet or both off common inlet or third sampler could alternate between being on and off common inlet
- Short- vs. long-term sampling comparison

GROUP IV

- Identify, do, and report QC used by group/method
- SOP with error propagation
- Group replicates for field precision
- Charge balance for H^+
- Mass balance for N(-III), N(V), S
- Acid to SO_4^{2-} ratio
- SO_4^{2-} concentration as flow check
- Flow audits before and during test
- Blind spiked filters (positive controls) as field and laboratory checks
- QA laboratory to check standards prior to testing to validate any stored or distributed materials
- Aerosol system to deliver known, spiked concentrations in field

Table 2 (Cont'd)

7. Site Selection and Time of Tests

GROUP I
- Eastern U. S. - use existing data base to find high acidity site
  - Penn State a possibility
- Summer and winter samples
- Western test if resources exist

GROUP II
- Do not do multicity study
- Use data from ongoing city studies (e.g., Harvard)

GROUP III
- May need to do field intercomparison twice in the summer
  - pure H_2SO_4-type site such as Parsons, WV, or Allegheny, PA
  - high NH_4NO_3, high acid, high HNO_3
- Field intercomparison probably cannot be done before summer 1990 because first need to do filter and chamber tests

GROUP IV
- Either one field test (East) and one laboratory shootout (RTP)
  - field test to identify field problems in summer and winter
  - laboratory shootout for controlled generation of range of conditions including humidity, photochemistry, haze, etc.
- Or two sites and two seasons (minimum) if H^+ and SO_4^{2-} is emphasis; West coast test is not required
- Emphasis is on first option

8. Merits of Laboratory vs. Field Testing

GROUP I
- Laboratory tests to resolve common issues
  - need to cool or not cool samples to preserve organic acids and prevent neutralization of strong acid during transport and storage
  - neutralization of H_2SO_4 by NH_4NO_3
  - filter media artifacts
- Chemical laboratory - tests of analytical techniques
  - liquid samples
  - filter deposits
  - matrix deposits
- Field comparison: benchmark
- Laboratory aerosol tests: resolve differences that cannot be reconciled from intercomparison data

GROUP II
- Comparison study is necessary - start in a controlled atmosphere (chamber) because ambient tests have too many variables
- After chamber tests, final test would be in field (for survivors of chamber tests)
- Data on sampler performance will validate methods
- EPA should provide add-ons to existing city studies for field test

Table 2 (Cont'd)

GROUP III

First do an intercomparison on H_2SO_4-doped filters (at various concentrations) sent to the laboratories

Second step should be a laboratory chamber study of H_2SO_4 at various concentrations and other conditions (some disagreed)

Field study to follow

GROUP IV

Field testing is a required practical test

Delivery system flow rates are the main (but minor) limiting factor to laboratory tests.

9. Reference methods

GROUP I

Prefer term benchmark methods

No reference methods are currently accepted

Primary standards for fine particle strong hydronium ion

GROUP II

Monitor chamber with flame photometric detector for sulfur, optical aerosol monitors, FTIR for gases, FTIR (by Johnson) desirable if available and inlet design checked

GROUP III

Continuous total particulate sulfur instument

GROUP IV

Generate $(NH_4)_2SO_4$, $(NH_4)HSO_4$, and H_2SO_4 standards of known particle size distribution to challenge samplers

Perhaps use radioactively labeled compounds

Infrared aerosol analyzer for continuous speciation

10. Other Concerns

GROUP I

Should still try to develop new instruments, e.g., continuous monitor for separate speciation of H_2SO_4 and $(NH_4)HSO_4$

Present technology is not an optimum technology

GROUP II

Chamber studies may also provide data relevant to health effects studies in chambers

GROUP III

Each phase should have results distributed and evaluated before going to next phase

GROUP IV

Not discussed

George Wolff stated that one issue brought up by two of the groups was the importance of being able to take historical measurements and compare them to one another. He expressed concern that, although it seems like a good idea, it could be difficult to make these comparisons because the methods have evolved over a period of years.

Robert Stevens noted that the preliminary laboratory tests may obviate any reason to go further with any sampling system with a substantial number of artifacts.

Paul Lioy added to George Wolff's comments. Lioy said that the laboratory tests may not provide answers about historical comparability because many of the older techniques did not use denuders or some type of preseparation. Atmospheres could not be reproduced in a way to reliably determine whether or not a technique was effective. Lioy felt it would be better to concentrate on developing new instruments than to spend much time evaluating historical ones.

George Wolff remarked that there appeared to be two views on one issue. One suggestion was to ensure that everyone has the same sampling heads to eliminate differences. The other suggestion was to keep everything the same as it is normally operated to try to compare previously collected data. Kenneth Knapp stated that Group III was one of those that made the suggestion for a common sampling inlet, but that the group also suggested additional samplers be used so they could be tested under normal operating conditions.

Ron Bradow stated that one idea discussed about data review started with the premise that any short-term field study is confined to the ranges of values present when that particular study is in the field. In fact, there is a very wide data base (at least for sulfate and ammonium ion) obtained from previous studies. These data might be useful in determining the effective range of measurements needed for ambient conditions and would have more significance for planning laboratory tests than field tests.

Leonard Newman raised two points. One was his strong conviction that any method deployed should be done in duplicate. He questioned Knapp's statement about triplicate instruments; Knapp had said that triplicate instruments would be divided, and include sampling at every 6-hours with another sampler taking 24-hour samples. Newman could see no justification for not performing each method in duplicate. Knapp replied that he meant triplicate as a minimum. In fact, the statistician in the group said to use four or five samplers. Knapp clarified that the group wanted to have a design where two instruments were operating one way and another operating another way, but it would be nice to have four instruments doing one operation and two doing something else. Knapp stated he understood what Newman was saying and that he was not in disagreement.

Leonard Newman added that his second point was that the purpose of the intercomparison is to devise a method to be used for monitoring. He was concerned about distraction from that purpose because the intercomparison is not a scientific investigation. The type of monitoring must be decided beforehand. If monitoring will be for 24-hour samples, then the intercomparison should be done with 24-hour samples. Do not complicate matters by having 6-hour samples. A method that might work for 6-hour sampling might be useless for 24-hour sampling. Knapp responded that flexibility has to be built in because no one has yet decided what the sampling period or the inlet cut will be. Discussions followed about whether the cut should be at 2.5, 2, 1.5, or 1 μm, etc.

Morton Lippmann stated that because there are so little data available on old methods, an intercomparison of these methods is not worth pursuing. It is important instead to use those methods now employed in health studies that will form the basis for future activities because those must be quantitative. If any group conducting health studies is doing something wrong, they should learn about it promptly because there will be quantitative dose-effect relationships resulting from those studies. Historical data on sulfates is of limited use; a data base on hydrogen ion is needed. Knapp added that this was considered in Group III, too, and the group felt that after finishing the intercomparison, the data could be compared to what investigators wanted to evaluate.

William Pierson disagreed with Morton Lippmann's assessment about the lack of data on hydrogen ion. He felt there are data on aerosol hydrogen ion available and that as long as there are any at all available, they should be used to help decide where to locate the field study. Knapp stated that there were two things involved here. The first is to choose the field site(s) based on as many currently known variables as possible. The second, which George Wolff discussed, is to design the comparison so that the results for instruments used earlier could be used to compare the resulting data bases.

Dr. Fred Lipfert elaborated on Leonard Newman's comment. If one accepts the premise that one is "qualifying a monitoring network" and "not conducting a scientific experiment," then it is essential to test in an urban area because that is where the full range of interfering particles is found. Kenneth Knapp responded that the idea had been discussed. The general consensus was to initially select an area where there was only one major pollutant. This would be followed by a second test in an urban area such as Zanesville, OH, if resources were sufficient.

Robert Stevens reinforced an issue of concern to several of the groups. He thought the measurement of hydrogen ion is only semiaccurate by itself. The mass balance between the hydrogen ion, ammonium ion, and sulfates ought to be part of the reporting aspect of this study. Although the hydrogen ion is associated with sulfate, reporting the mass balance adds integrity and internal consistency to the measurement. Knapp noted that the consensus of his group was to focus on the hydrogen ion and sulfate ion on the aerosol, as the minimum. However, they did not wish to discard the other data obtained. Thus, a single group conducting many other analyses perhaps would provide insight into variability. Knapp's group did say to measure all species, but not necessarily by the techniques used by the individual groups. However, another group added that research methods should not be used and single techniques should be employed.

Petros Koutrakis raised a point that had been mentioned in Group I. Different people report different hydrogen ion concentrations because they use different starting extraction solution pH or they use Gran titration. The differences in protocols need to be addressed before testing starts. Otherwise, someone can say that the reason they have more acidity is because the extraction pH is 0.4. One suggestion was to have multiple (e.g., three) samples, give one to a group doing total acidity (such as by Gran titration), to compare one method with another. Knapp felt that was a good point. He emphasized that part of the protocol must be to establish what units should be reported, and participants must adhere to that. Jed Waldman mentioned that the issue of laboratory analytical differences needs to be resolved separate from, and prior to, any chamber and field studies.

George Thurston asked for a clarification. If many ions are collected, that might imply that many variables will be used to evaluate differences, but that is not stating how to evaluate the instruments. The evaluation will be made on some predetermined measure of particulate acidity. Knapp answered by saying yes, and that measure is whatever is decided in the protocol. George Thurston then gave as an example a case where a dichotomous sampler is used to collect samples. He stated it would be acceptable to have the nitrate partially lost as long as the hydrogen ion was accurately measured. Thus, although it might be interesting that nitrate is gone, it is not critical.

Ron Bradow noted that he heard someone say that this study was not a scientific study, but a comparison of potential monitoring devices for use in the field. In that case, it is almost certain there will be some systematic differences. Measurements of acid gases, ammonia, and any of the other species are useful specifically as diagnostic tools to resolve the reasons for those differences.

SECTION 13

CONCLUSIONS

INTRODUCTION

William Wilson noted that EPA planners of the intercomparison have good ideas to work with; EPA would determine median consensus and consider the comments from the fringes when the detailed planning begins. EPA has a limited schedule to do what is necessary and may not have 2 to 3 years to accomplish the tasks desired in a slow, careful scientific approach.

PANEL DISCUSSION

Paul Lioy summarized consensus items in discussion on the field and other comparisons of acid aerosol measurement techniques. He also offered his own opinions about future directions because of the importance of developing a future ambient air quality standard. At present, hydrogen ion is the best indicator available for measuring particle acidity. However, measuring sulfuric acid and ammonium bisulfate simultaneously in a continuous analyzer would provide the best data possible for assessing compliance and determining if acute effects can occur from ambient exposures, in addition to those from chronic exposures.

Development of a systematic approach for evaluation was agreed upon. All researchers involved in a performance test should have their analytical laboratories validated or meet some established performance measure. Some laboratory experiments are needed prior to field evaluation. A level of effort somewhere between what Group III and Group II recommended would be reasonable. During the laboratory intercomparisons, duplicate samples should be collected for each technique. Unusual things can happen in the field, but with duplicate samples under controlled conditions, a good estimate of precision is obtained.

Although difficult, Lioy would support field studies but only if two other steps are done beforehand to develop a logical approach to understanding acidity. He also thought that field performance tests require a steering group to make sure that everything is planned and implemented properly. Operation protocols should be specified by preagreement and provided to a third party for review. He expressed concern about site selection and suggested that the choice be based on the best location for examining acidic particles under the greatest range of possible concentrations. He did not favor going to an urban area first because it would increase the complexity of an already difficult task. Although he favored tests in an urban area at some point, he felt that a more crucial first step was understanding instrument performance.

Lioy felt that older instrumentation could be included in the initial laboratory intercomparison. If the instruments performed reasonably well, they could be included in the field study. Also, if some consistency with older data is found, there is a better likelihood of using the older data in the development of the final criteria document for acid aerosols.

Lioy was uncertain about the selection process for participants. Successful operation during the initial phases would be one component, but some unusual techniques, such as continuous methods, might require more flexibility initially. He felt that the laboratory studies are important, because spiked samples cannot be sent to a group using a continuous analyzer. These groups should have an opportunity to participate in Phase II and be provided with a second chance to eliminate any ambiguities in their analyses.

Lioy felt that the workshop groups did an excellent job and showed much consistency among their approaches. He was hopeful that an intercomparison of techniques and field applicability could provide a basis to decide whether EPA could have a useful instrument, i.e., an instrument suitable for routine field monitoring of fine-particle aerosol acidity by state agencies.

George Wolff felt that this workshop had accomplished its goals and objectives. Rather than review many of the points already made, he emphasized a few others. He thought that the protocol that the CARB established could be refined with many of the ideas from the workshop to obtain the best QA intercomparison that has existed to date.

Wolff's main point was to take the time and do this study right, regardless of EPA's preferred timetable, so that once the issue returns to CASAC it is not given back to EPA again. He recommended that simple systems be examined too because it is not easy to develop a system that is both easy and reliable. Minor modifications in a dichotomous sampler (e.g., using a simple denuder followed by a filter) and including simple systems in the evaluation seems worthwhile. EPA should try to brainstorm on which simple systems might work on a routine basis and could be developed for inclusion in this intercomparison.

John Spengler noted the tendency for atmospheric scientists to be very demanding of their own systems. But, ambient measurements are only a surrogate for exposure; today's methods have smaller uncertainties than those concerning human exposure. However, researchers should still try to improve techniques and try hard to eliminate any existing systematic differences.

Spengler recommended that the same scrutiny of an intercomparison be applied to the clinical investigators. He noted that these investigators rarely compare methods and procedures even for health end points, subject variation, subject reactivities, pollutant delivery systems, size distributions, and measurements to determine concentration. Looking at the variety of work that is already published from Spektor, Linn, Avol, Hackney, Utell, Korn, and Horstman, the clinical studies effects levels range between 1,000 to 50,000 nmol hydrogen ion delivered. If an intercomparison was done tomorrow, Spengler felt there would be more agreement among the workshop participants than among the researchers using health end points. In the intercomparisons and the methods evaluations, the talent and experience of the physical scientists must be applied to both sides of the equation. It will take both the exposure and health assessments to better define the need for an ambient air quality standard and what level is acceptable.

Doug Lawson stated that he really preferred the phrase "methods evaluation study" to "intercomparison." He thought that the studies were scientifically valid because they involved understanding how samplers work and also understanding chemical equilibrium dynamics in a very complex system.

Lawson next discussed briefly three points about CARB programs. He noted that CARB has a 5-year acid deposition program totalling $15 million including health effects studies. He also mentioned that CARB has a contract with Desert Research Institute to initiate an acid aerosol and gas monitoring network of 10 stations for California. Lawson commented that it is critically important to have good communication between the health effects community and those who are making the ambient measurements. He noted that California is investigating both gas- and particle-phase components. He felt that the question of how important or unimportant acid gases are for health effects was just speculation because the work has not been done. However, he thought it an important issue because in neutral or mildly alkaline body fluids weak acids readily dissociate to donate hydrogen ion.

Next, Lawson presented nine important items to consider in conducting an intercomparison for acid aerosols:

1. Have a clearly defined objective in mind for the study.

2. Have good quantification of error or error bars associated with the numbers.

3. Consider the potential influence of ammonia and ammonium ion on health effects and their role in the system dynamics of particle/gas/sampler interactions.
4. Ensure that the person who runs the study has no preconceived ideas as to who is right. This person should have absolutely no involvement in the development of any of the samplers for the study.

5. Do the study in an area with high enough concentrations. Some variability in ambient conditions would be desirable too.

6. Emphasize concern about the overall character and measurement of hydrogen ion. There appears to be a need to have those people who understand concepts of acidity included in discussions. These people (such as Howard Liljestrand) need to consider thoroughly some of the issues raised here such as pH vs. strong acidity, different end points or Gran titration, etc.

7. Keep replicate samplers within the study.

8. Consider costs. The cost of the 1985 or 1986 shootouts was about $1 million including in kind contributions. About $50,000 is needed for a group for about a week of sampling. Also make sure there is adequate power at the site.

9. Keep the big picture in mind. Try to look at total atmospheric acidity. In shifting from acid rain to acid particles, keep a broad view because a relatively small amount of money in such a study can provide information on significantly more pollutants if the study is designed appropriately.

Lawson commented that it is also important to have routine samplers in the study to relate the detailed measurements to the routine measurements. In material shown earlier, there were huge differences between a quantity called "true particulate nitrate" and routine high-volume sampler nitrate data. Provisions must be made for technology transfer.

Morton Lippmann commented on a few differences among the four group reports. First, he called attention to a journal to be distributed soon consisting of the proceedings of a 1987 meeting on the health effects of acid aerosols. It was scheduled to appear in Volume 79 of Environmental Health Perspectives (February 1989). It is an excellent summary of the state of the art of what is known about acid aerosol health effects and contains about 32 presentations by all the most active researchers in the field. He then noted the remarkable similarity among the major objectives that participants identified and the important caveats for these exercises. The one major difference was on emphasis of laboratory calibration with field verification vs. emphasis on field evaluation supported by laboratory evaluation. His personal preference is the former, but perhaps the objectives can be accomplished either way. By consensus, the first objective is obtaining an accurate and reliable method for measuring particulate strong acid that is as free as possible from interferences. A second objective is assurance that what the current field epidemiology groups are doing is right and, if not, that what they have done can be corrected for use in quantitative exposure response relationships.

Lippman noted that there was a strong consensus for the need for third party activity. However, he felt that there should be no single third party. Instead there should be a series of contracts with independent parties expert in special areas such as the University of Minnesota in the area of laboratory chamber evaluations. Enough samples should be collected in replicate so that duplicate analyses can be done by the third party laboratory and by the individual investigators.

Lippmann had a slightly different emphasis than some of the other participats concerning the issues of field testing and site selection. Testing may be more complicated in the center city, but it is also not a good location because of generally lower acidity. Acid levels are much more likely to be higher outside the center city, and a continuing emphasis on center city sampling when it is used for a primary ambient air quality standard that is health driven does not make sense. So, even though the population is less dense, more people need protection in areas around the cities and in more remote areas downwind wherever secondary air pollutants are higher. This makes site selection among candidate cities in Harvard's multicity study even more sensible because it can be done more efficiently. Instruments can easily be added to a site that is currently operating.

John Haines felt that EPA would have to begin immediately to plan the studies and implement the recommendations of this workshop. He felt that it was important to be able to compare the results of the ongoing epidemiological studies and, thus, one should proceed as rapidly as possible to get these comparison studies under way. He also thought it important to bring some simplified systems into the study to allow monitoring on a broader geographic basis and provide more data to help in reaching determinations on the standard-setting process.

William Wilson agreed that EPA will have its work cut out for it and that events should proceed as rapidly as possible in a good scientific manner. The EPA staff will be evaluating all the advice, information, and ideas that came from this workshop in order to plan the next phase of this study.

Discussion

In response to a question about the time frame for the next steps in the methods evaluation, Wilson replied he would try to give information about EPA's plans in the cover letter to accompany the workshop report. The next steps are not clear because the issue of funding for this year still needs to be clarified. Until it is, one cannot say how rapidly the next steps can be taken.

BIBLIOGRAPHY

Clean Air Scientific Advisory Committee. 1988. Recommendations for Future Research on Acid Aerosols. EPA-SAB/CASAC-89-002, U.S. Environmental Protection Agency, Washington, D.C. 14 pp.

Hering, S.V., Lawson, D.R., Allegrini, I., Febo, A., Perrino, C., Possanzini, M., Sickles, II, J.E., Anlauf, K.G., Wiebe, A., Appel, B.R., John, W., Ondo, J., Wall, S., Braman, R.S., Sutton, R., Cass, G.R., Solomon, P.A., Eatough, D.J., Eatough, N.L., Ellis, E.C., Grosjean, D., Hicks, B.B., Womack, J.D., Horrocks, J., Knapp, K.T., Ellestad, T.G., Paur, R.J., Mitchell, W.J., Pleasant, M., Peake, E., MacLean, A., Pierson, W.R., Brachaczek, W., Schiff, H.I., Mackay, G.I., Spicer, C.W., Stedman, D.H., Winer, A.M., Biermann, H.W., and Tuazon, E.C. 1988. The nitric acid shootout: field comparison of measurement methods. Atmos. Environ. 22(8):1519-1539.

National Institute of Environmental Health Sciences. 1989. Symposium on the Health Effects of Acid Aerosols in Research Triangle Park, North Carolina, 1987. Environ. Health Perspect. 79:1-321.

Schwartz, S.E., and Tanner, R.L. 1976. Validation of Methods for Determination and Speciation of Sulfate Aerosols. Brookhaven National Laboratory, Upton, New York, 23 pp.

APPENDIX A

AGENDA

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Atmospheric Research and Exposure Assessment Laboratory
Research Triangle Park, NC 27711

AGENDA

ACID AEROSOL MEASUREMENT WORKSHOP
FEBRUARY 1-3, 1989

Wednesday, February 1

TIME	**TOPIC**	**SPEAKER**
8:30 a.m.	Introduction (Welcome, Background, Overview)	Foley/Wilson
	Review of Acid Aerosol Health Effects Data	Graham
	Overview of CASAC Research Recommendations	Lippmann
	The Use of Measurement, Exposure, and Health Effects Data in Assessing Health Risks	Lounsbury
10:00 **BREAK**		
10:30 a.m.	Overview of Current Acid Aerosol Measurement Programs	
	Harvard School of Public Health	Spengler
	R. W. Johnson Medical School	Lioy
	Environment Canada	Wiebe
	Electric Power Research Institute	Mueller/Wyzga
	California Air Resources Board	Lawson
	Brookhaven National Laboratory	Newman
12:00 **LUNCH**		
1:30 p.m.	Current Acid Aerosol Measurement Techniques	
	Harvard School of Public Health	Koutrakis
	R.W. Johnson Medical School	Waldman
	Environment Canada	Wiebe
	California Air & Industrial Hygiene Lab	Appel
	Brookhaven National Laboratory	Tanner
	Argonne National Laboratory	Johnson
	AREAL, U.S. EPA	Stevens
3:30 **BREAK**		
4:00 p.m.	Selecting Acid Aerosol Indicators	
	Overview	Wilson
	Panel Discussion: Key Factors to be Considered	
	Panel Members: Grant, Lippman, Morris, Spengler, Wiebe, Wolff	
5:00 p.m.	End of Day 1 Formal Sessions	

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AGENDA

Thursday, February 2

TIME	TOPIC	SPEAKER
8:30 a.m.	Overview of Panel Discussion on Selecting Acid Aerosol Indicators	Stevens
8:45 a.m.	Group Discussions on Selection of Acid Aerosol Indicators Participants will divide into 4 groups; each group will make recommendations about the following: • indicators for characterization and exposure studies • indicators for health studies • indicators for indoor studies • indicators for fixed site monitoring • pH vs titratable acid • need to measure SO_4^- and NO_3^- • need to measure acid gases (e.g., HNO3, HNO2, NH3) • measurement frequency, duration, averaging time	
11:00 a.m.	Group Reports Summary	 Stevens
12:00 LUNCH	Pickett Suite Hotel (all workshop participants)	
1:15 p.m.	Data Quality Objectives for Acid Aerosol Measurements	Foley
1:35 p.m.	Design of Comparison Studies	
	Overview	Knapp
	Review of Previous Methods Comparison by CARB	Lawson
	Review of Previous Methods Comparison in Italy	Allegrini
2:15 p.m.	Group Planning: Design of Laboratory and Field Methods Testing and Comparison Program Participants will divide into 4 groups: each group will plan a program that will address at least the following areas. • review objectives • participants • species to be measured • measurement frequency, duration, and averaging time • data analysis and reporting • QA/QC • site selection and time of tests • merits of laboratory vs field testing • reference methods	
5:00 p.m.	End of Day 2	

AGENDA

Friday, February 3

TIME	TOPIC	SPEAKER
8:30 a.m.	Group Reports on Design of Laboratory and Field Testing Programs	
	Summary	Knapp
9:45 BREAK		
10:00 a.m.	Workshop Closure	Wilson
	Panel Discussion: Issues and Action Items for Comparative Testing of Acid Aerosol Measurement Methods	
	Panel Members: Haines, Lawson, Lioy, Lippmann, Spengler, Wolff	
	Summary	Wilson
11:30 a.m.	End of Workshop	

APPENDIX B

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February 1-3, 1989

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APPENDIX C

GROUP ASSIGNMENTS

ACID AEROSOL MEASUREMENT WORKSHOP

Group Assignments

GROUP I (NC ROOM)	GROUP II (RALEIGH ROOM)	GROUP III (DURHAM I)	GROUP IV (DURHAM II)
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APPENDIX D

SUMMARY OF ACID AEROSOL SAMPLERS/PROTOCOLS

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APPENDIX D

SUMMARY OF ACID AEROSOL SAMPLERS AND PROTOCOLS

INTRODUCTION

Three groups in the United States are conducting measurements of ambient acid aerosols on a routine basis in support of epidemiological studies that include the health effects of acid aerosols: Harvard School of Public Health, Robert Wood Johnson Medical School, and New York University Institute of Environmental Medicine. This appendix briefly summarizes the four systems in use by these groups: the Harvard Impactor System, (HIS), the Harvard-EPA Annular Denuder System (HEADS), the Robert Wood Johnson Medical School Annular Denuder System (ADS), and the New York University Sequential Acid Aerosol Sampling System (SAASS).

THE HARVARD IMPACTOR SYSTEM

Sampler Design

The HIS consists of an impactor to remove particles with aerodynamic diameter above 2.5 μm, a honeycomb denuder coated with citric acid/glycerol to remove ambient ammonia, and a Teflon membrane filter to collect the sample. A pump unit maintains a flow of 4 lpm, and a 7-day timer allows programmed start and end times for the 24-hour sample collection period.

The impactor has been described previously (Turner et al., 1985). The diffusion denunder at the sampler entrance is constructed using an aluminum foil laminate honeycomb. The honeycomb surface is etched with ethanolic potassium hydroxide to retain more of the denuder coating. The denuder is coated with an ethanol solution containing 4% (w/v) citric acid monohydrate and 3% (w/v) glycerol. The 2-μm pore polytetrafluoroethylene (PTFE) Teflon membrane filters were chosen for low blank acid and sulfate concentration and are bonded to polyvinyl chloride (PVC) square holders.

Sample Transport and Handling

After the impactor is removed from the pumping unit at the sampling site, caps are placed on both the inlet and outlet ports and the units transported to a field laboratory. There the sealed unit is placed inside an ammonia-free glove box that contains citric acid-coated filter paper (Whatman No. 1). Once the impactor is inside the glove box, the filter holder is removed and placed inside a small polystyrene box that also contains two citric acid-coated cellulose filter papers separated from the sample filter by PVC spacers, with one uncoated cellulose filter below the coated ones. The polystyrene boxes are placed inside another polystyrene foam box with additional pieces of citric acid-coated filter paper and shipped to the central laboratory for analysis.

At the central laboratory, the filters are kept inside the polystyrene foam shipping box until ready for pH analysis. The small polystyrene boxes are removed from the shipping box and placed inside an ammonia-free hood when preparing for extraction. Citric acid-coated glass wool removes ammonia and ambient particles from the supply air to the hood.

Analysis

Inside the hood, the membrane filter is cut from its holder and put inside a 4-ml polystyrene cup. The filter is wetted with 0.1 ml of ethanol. Then 3 ml of an aqueous extraction solution containing

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10^{-4} N perchloric acid and 0.04 M potassium chloride is added to the cup. The capped cups are sonicated for 15 minutes with the cup holder rotated 90° every 5 minutes.

Two 1-ml aliquots of extract are transferred to 2-ml sample cups for pH analysis. The remaining 1 ml is stored at 5 °C for sulfate analysis later. Hydrogen ion standards are prepared, using sulfuric acid, in a range equivalent to 0-550 nmol/m^3 of hydrogen ion (for 24 hours at 4 lpm). Standards are prepared by adding 0.100 ml of relatively concentrated solution of sulfuric acid in ethanol to 3 ml of extraction solution. Blank solvent is prepared using with the same ratio of pure ethanol to extraction solution.

The pH determinations are performed with an Orion Model 611 pH meter and a Fisher Scientific Model E-5M combination microelectrode. The pH of standards and filter extracts is tested by using a 2-ml cup containing 1 ml of solution to rinse the electrode and another 2-ml cup to determine pH. Two 2-ml cups of blank solvent are measured between tests, the first to rinse the electrode and the second as a control. The apparent hydrogen ion concentration, $[H^+]$, is calculated for each standard and filter using the following equation:

$$[H^+] = 10^{-pH} - 10^{-pHb}$$

where pH is the pH of the test solution and pHb is the pH of the blank solvent.

Apparent concentrations may differ slightly from true concentrations because of ionic strength effects caused by the 0.04 M potassium chloride and possibly by the 3% ethanol. Apparent concentrations are regressed on actual standard concentrations and the slope of the resulting curve used to determine actual sulfuric acid equivalent concentrations for ambient air filter extracts. Because strong acid contractions determined for doped filter standards were about 3% lower than those for routine standards and because routine standards are prepared without filters, a correction is made for the difference when calculating the concentration for filter extracts. Final sample concentrations are determined from actual flow and sample times.

The estimated minimum detectable concentration is 2 nmol/m^3 (0.2 μg/m^3) of sulfuric acid. Sulfate is measured using the methylthymol blue method with a Technicon Auto Analyzer II (McSwain and Watrous, 1974).

References

Koutrakis, P., Wolfson, J.M., and Spengler, J.D. 1988. An improved method for measuring aerosol strong acidity: Results from a nine-month study in St. Louis, Missouri and Kingston, Tennesee. Atmos. Environ. 22:157-162.

McSwain, M.R. and Watrous, R.J. 1974. Improved methylthymol blue procedure for automated sulfate determinations. Analyt. Chem. 46:1329-1331.

Turner, W., Spengler, J.D., and Marple, V.A. 1985. Indoor aerosol impactor. In: Proceedings of the Fifth Annual National Symposium on Recent Advances in Pollution Monitoring of Ambient Air and Stationary Sources. EPA-600/9-85-029, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. pp. 158-165.

THE HARVARD-EPA ANNULAR DENUDER SYSTEM-I

Sampler Design

This version of the HEADS is designed to assess effects on the measurement of atmospheric aerosol acidity due to losses from interactions of collected particles. It consists of a glass impactor, three annular denuders, and a filter pack. The impactor has a theoretical 50% aerodynamic particle cutoff point of 2.5 μm and an actual cutoff point of 2.1 μm at a flow of 10 lpm. Gaseous sulfur dioxide, nitric acid, and nitrous acid are trapped by a sodium carbonate-coated annular denuder. A second sodium carbonate- coated annular denuder is used to determine artifact formation of nitrate and nitrite to correct for the apparent concentration of nitric acid and nitrous acid on the first dunuder. The third denuder is coated with citric acid to collect gaseous ammonia. The denuders are followed by a filter pack containing four 47-mm diameter filters. The first filter is a 2-μm pore PTFE Teflon membrane filter (Gelman Sciences) to collect fine particles for aerosol strong acidity, ammonium, sulfate, nitrate, and nitrite determinations. The second filter is a cellulose filter (Millipore) treated with 2% (w/v) sodium carbonate and 2% (v/v) glycerol in 3:10 methanol/water solution. This filter traps nitric acid arising from the dissociation of ammonium nitrate collected on the Teflon filter and from the displacement of the sulfate-related hydrogen ion by ammonium nitrate. The third filter is another sodium carbonate-treated cellulose filter to correct for artifact nitrate formed in situ due to the interaction between nitrogen oxides and/or PAN with the sodium carbonate-treated cellulose filter. The nitrate concentration on the first sodium carbonate-treated filter can be corrected by subtracting the nitrate concentration on the second sodium carbonate-treated filter.

The fourth filter is a citric acid-coated cellulose filter to trap ammonia from the dissociation of ammonium nitrate collected on the Teflon filter. Using this filter pack system, the apparent aerosol strong acidity measurements can be corrected by adding the moles of corrected nitrate and nitrite from the first cellulose filter and subtracting the moles of ammonia measured on the citric acid-treated filter.

THE HARVARD-EPA ANNULAR DENUDER SYSTEM-II

Sampler Design

This version of the HEADS is a simpler one designed to collect acidic aerosols and gases without quantifying corrections due to losses from interactions of collected particles. The system consists of a borosilicate glass impactor, two glass annular denuders, and a fluorinated ethylene-propylene (FEP) Teflon filter pack containing a Teflon filter and a sodium carbonate-coated glass fiber filter. The sampler operates at a flow of 10 lpm. A schematic diagram of the system and illustration of the impactor has been published (Koutrakis et al., 1988)

The impactor consists of an entrance elutriator containing an inlet tube followed by an acceleration jet and an impaction plate. The impaction plate is a porous glass disk impregnated with mineral oil and is mounted at the entrance to the first annular denuder. The impactor is designed to have a 50% aerodynamic cutoff point at 2.5 μm at a flow of 10 lpm, but has a measured cutoff point of 2.1 μm.

The design of the two annular denuders is similar to that of others (Vossler et al., 1987). The first denuder has a length of 26.5 cm, and 21.5 cm for the inner cylinder. The outer diameter of the inner cylinder is 2.20 cm, and the thickness of the annulus is 0.10 cm. The second cylinder has a length of 24.2 cm for the outer cylinder. The other dimensions are the same as for the first denuder. The denuders are coated with a 10-ml solution containing 1% (w/v) sodium carbonate and 1% (v/v) glycerol in a 1:1 mixture of methanol and water. The first denuder collects sulfur dioxide, nitric acid, and nitrous acid. The second denuder measures artifact nitrate and nitrite to correct nitric and nitrous acid concentrations on the first denuder.

Following the second denuder is an FEP Teflon filter pack containing two filters and stainless steel support screens. The first filter is a 47-mm diameter PTFE 2-μm pore Teflon membrane, with a polyolefin ring (Gelman Sciences), that collects fine particles and is used to determine mass, sulfate, nitrate, and nitrite. The second filter is a 47-mm diameter glass fiber filter (Millipore) coated with 2% (w/v) sodium carbonate in 3:10 methanol/water solution. The carbonate filter traps nitric and nitrous acid.

Handling and Analysis

After sampling, the denuders are extracted with 10 ml of ultrapure water and the extracts stored at 5 °C and later analyzed for anions by ion chromatography using a Dionex Model 4000i. The filter pack is opened in an acid gas-free hood. The sodium carbonate-coated filter is placed in a vial with 5 ml of ultrapure water and sonicated for 15 minutes. The extract is also analyzed for anions by ion chromatography. After equilibration, Teflon filters are weighed twice, cut, and then placed inside a polycarbonate vial. The filter is wetted with 0.100 ml of ethanol before extraction. The same extraction and analysis procedures are then used for the Teflon filter as for the coated filter.

References

Koutrakis, P., Wolfson, J.M., Slater, J.L., Brauer, M., Spengler, J.D., Stevens, R.K., and Stone, C.L. 1988. Evaluation of an annular denuder/filter pack system to collect acid aerosols and gases. Environ. Sci. Technol. 22:1463-1468.

Vossler, T.L., Stevens, R.K., and Baumgardner, R.E. 1987. A Study of the Performance of Annular Denuders and Preseparators. In: Proceedings of the 1987 EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, North Carolina. pp. 168-171.

THE ROBERT WOOD JOHNSON MEDICAL SCHOOL ANNULAR DENUDER SYSTEM (ADS)

Sampler Design

The ADS consists of an inlet with an impactor preseparator having an aerodynamic diameter cutoff point of 2.5 μm, three annular denuder tubes, and a three-stage filter pack. A pump unit maintains a flow of 10 lpm, and a 7-day timer allows programmed start and end times. ADS samples may be run for 8, 12, or 24-hour durations or in cycled operation (e.g., 10 minutes on/50 minutes off for 7-day periods).

The inlet is a Teflon-coated aluminum elutriator tube with an accelerator nozzle. Different diameter accelerator jets are available. The impaction surface is a frit made of either porous ceramic material or stainless steel coated with 50 μl of a 1% (v/v) solution of silicone oil in toluene.

The annular denuder tubes consist of two concentric glass tubes creating a 0.1-cm annulus. The inner surfaces are etched to provide greater surface area for the coating solution. The dimensions for all three denuders are the same. The outer tube is 24.2 cm long. The inner cylinder is 21.7 cm long and is 3.8 cm in diameter, leaving an annulus of 1 mm. The first two annular denuders are coated with 1% (w/v) sodium carbonate and 1% (v/v) glycerol in a 1:1 solution of methanol and deionized water. The first denuder measures gaseous sulfur dioxide, nitric acid, and nitrous acid. The second denuder is used to determine artifact formation of nitrate and nitrite and to correct the apparent concentrations on the first denuder. The third denuder is coated with 1% (w/v) citric acid and 1% (v/v) glycerol in a 1:1 solution of methanol and water. The third denuder is used to collect gaseous ammonia.

The annular denuder tubes are followed by a three-stage filter pack containing 47-mm filters supported by stainless steel screens and separated by polyethylene spacer rings. The first filter is a 2-μm pore-size Teflon membrane filter, Zeflour (Gelman Sciences), followed by a 1-μm pore-size nylon membrane filter, Nylasorb (Gelman Sciences), and then a citric acid-impregnated, glass fiber filter, and a prefilter-pad, type AP filter (Millipore). The glass fiber filter is impregnated with 1.0 ml of a 2% (w/v) citric acid solution in ethanol. The Teflon filter collects fine particles. The nylon second filter traps nitric acid arising from the dissociation of ammonium nitrate or nitric acid collected on the Teflon filter. The citric acid-impregnated, glass fiber filter retains ammonia. The three filters together can give unbiased measures of aerosol nitrate and acidity. The blank-corrected apparent acidity on the Teflon filter can be corrected by adding the blank-corrected nitrate concentration of the nylon filter and subtracting the blank-corrected ammonium concentration on the glass fiber filter.

Handling and Analysis

Following each run, the ADS assembly is removed from its field housing, its ends capped, and brought back to the laboratory. In the laboratory, the assembly pieces are uncoupled and capped. The denuder tubes are extracted with water. Filters are unloaded from the filter pack and either directly extracted or stored in a petri dish for extraction later. A glove box, lined with citric acid-soaked paper, is used to maintain an ammonia-free atmosphere.

Each run generates six sample aliquots. Anions are analyzed by ion chromatography (either Waters or Dionex systems). Ammonium ion is analyzed by the indophenol method using an autoanalyzer. Hydrogen ion, or strong acidity, is analyzed by an acid addition method using pH determination.

To extract the Teflon filter, it is placed in an extraction vessel, membrane side down. The filter is wetted using 0.2 ml of methanol, and then 10.0 ml of 5 x 10^{-5} M perchloric acid in deionized water is added. Containers with the filters are put on an orbital shaker for 1 hour. The extraction solution is then decanted into a container.

Acidity determinations are made using pH measurements of the extracted filters. Aliquots of 1 ml are put in polystyrene vials. The ionic strenth of aliquots is made constant (0.02 M) with a spike of 20 μl 1 M potassium chloride stock solution. Filter acidities are calculated from standards made with sulfuric acid. The standards range from 0 to 400 μequiv/l of sulfuric acid. A pH meter is used to measure the pH of the filter extract. For each batch of filter extracts, a calibration curve is calculated using the mean pH of each standard reading taken before and after the batch.

Loss of volatile nitrate species from the Teflon filter may occur. These volatilized components are collected on the nylon and citric acid-impregnated backup glass fiber filters. The blank corrected nitrate concentration on the nylon filter is due to both nitric acid and ammonium nitrate; the blank-corrected ammonium ion concentration on the glass fiber filter is due to only ammonium nitrate. The acidity correction is due to nitric acid and is calculated as the difference of nylon filter nitrate less glass fiber filter ammonium.

Reference

Waldman, J.M. 1988. Standard Operating Procedures: Atmospheric Acidity Studies Using the Annular Denuder (Draft 2.3). Robert Wood Johnson Medical School, University of Medicine & Dentistry of New Jersey, Piscataway, New Jersey. 39 pp.

THE NEW YORK UNIVERSITY SEQUENTIAL ACID AEROSOL SAMPLING SYSTEM

Sampler Design

The SAASS has been designed to collect an uninterrupted sequential series of daily acid aerosol samples. The SAASS consists of a series of sampler units. Each sampler unit consists of a nitric acid denuder, an ammonia denuder, a dual impactor with two plates each having a 2.5-μm aerodynamic diameter cutoff point, and a filter pack containing a 37-mm Teflon filter and a 37-mm nylon filter. The flow rate through the unit is 4 lpm.

The dual impactor is the same as the one used in the HIS (Koutrakis et al., 1988) and designed by Marple (Marple et al., 1987). The impaction plates are coated with a neutral mineral oil (Petrolatum NF) after weekly cleanings to reduce particle bounce problems.

The impactor/denuder design used is similar to that used by the HIS (Koutrakis et al., 1988) except that an additional honeycomb denuder precedes the ammonia denuder to remove ambient nitric acid before the filter sample. In addition, a nylon filter follows the Teflon filter to collect nitrate volatilized from the Teflon filter and allow total particulate nitrate to be determined. The 37-mm Teflon filter (Anderson) is polyethylene backed and has a 2-μm pore size. The Nylasorb 37-mm nylon filter (Gelman Sciences) has a 1-μm pore size. The upstream nitric acid denuder is the same as the ammonia denuder in the HIS (Koutrakis et al., 1988), except that it is coated with a 1% sodium carbonate solution before being shipped to the field.

The SAAS automatically initiates each sample and controls the sample start time, duration, flow rate, and end time as it records each sample's elapsed time and flow rate. The 4.0 lpm pump is regulated by a flow controller, and the flow is directed through each sampler unit sequentially by automatically controlling the opening and closing of flow control solenoid valves downstream of each unit. The sampler units are usually left in the ambient air for a week during which they sample for 1 day. However, the ammonia denuder has enough reserve capacity to protect the sample for the remainder of the week under no-flow conditions.

Sample Transport and Handling

After a sampling week is complete, field operators cap the sampling units, with samples inside, and ship them back to the control laboratory. There the filters are removed under an ammonia-free hood and then stored in an ammonia-free environment until analysis.

Analysis

The ion analyses of sample filters, field blanks, and positive controls involve nitrate, sulfate, and ammonium ions and are performed by ion chromatography. Strong acidity is determined using the pH method documented by Harvard (Koutrakis et al., 1988). However, an Orion Model 611 pH meter with log-R compensation is used with a Ross Model 816300 combination probe. A Model 4000i Dionex ion chromatograph unit is used to analyze for other ions.

References

Koutrakis, P., Wolfson, J.M, and Spengler, J.D. 1988. An improved method for measuring aerosol strong acidity: Results from a nine-month study in St. Louis, Missouri and Kingston, Tennessee. Atmos. Environ. 22:157-162.

Marple, V.A., Rubow, K.L., Turner, W., and Spengler, J.D. 1987. Low flow rate sharp cut impactors for indoor air sampling: Design and calibration. J. Air Pollut. Control Assoc. 37:1303-1307.